Volume 20 Number 2
February 1950

JOURNAL OF GENERAL CHEMISTRY of the USSR

ЖУРНАЛ ОБЩЕЙ ХИМИИ
(ZHURNAL OBSHCHEI KHIMII)

TRANSLATED FROM RUSSIAN

CONSULTANTS BUREAU, NEW YORK

THE JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Vol. 20, 1950

FEB

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU
153 West 33 Street, New York 1, N. Y.

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THE JOURNAL OF GENERAL CHEMISTRY OF THE U.S.S.R.

Vol. 20, (1950)
No. 2 (February)

Publication of the Academy of Sciences of the U.S.S.R.

IN ENGLISH TRANSLATION

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CONSULTANTS BUREAU

153 West 33 Street
New York 11, N. Y.

Printed in the United States of America

Annual Subscription $95.00. Single issue $12.00

PATTERNS OF CHANGE IN SOLUBILITY

III. ENERGY CHARACTERISTICS OF ISOTHERMS IN MULTICOMPONENT SYSTEMS

E. I. Akhumov and N. S. Spiro

1. INTRODUCTION

In our research on solubility polytherms we have developed [1,2] the energy characteristic—deviation of the actual equilibrium from the ideal equilibrium, as calculated from the law of mass action for eutonic points.

The present paper deals with the problem of the change of the derived equilibrium constant and of the free energy for isotherms.

2. BASIC NOTATION

Let us take a three-component water-salt system, say with the like anion R^{-r}:

$$M_rR_m - N_rR_n - H_2O, \qquad (1)$$

where M^{+m} and N^{+n} are the cations.

TABLE 1
Basic Notation

	General form	Components "1"	Components "2"
Individual solubility...	L	L_1	L_2
Mutual solubility.....	C	C_1	C_2
Joint solubility at the eutonic point.....	r	r_1	r_2
Reduced equilibrium constant for isotherms....	$\bar{\varphi}$	$\bar{\varphi}_1$	$\bar{\varphi}_2$
Reduced equilibrium constant for polytherms...	φ	φ_1	φ_2
Change in free energy for isotherms.....	$\Delta\bar{F}$	$\Delta\bar{F}_1$	$\Delta\bar{F}_2$
Change in free energy for polytherms	ΔF	ΔF_1	ΔF_2

Let us assume that under these conditions no chemical compounds are formed between the components that constitute the solution.

In the given case, the solubility isotherms will consist of two branches, corresponding to the solid phases M_rR_m and N_rR_n, which meet at the eutonic point.

The basic notation for salt solubilities (in mols per 1000 mols of water or in grams per 1000 g of water) and for other variables are listed in Table 1.

3. Values of the Reduced Equilibrium Constants and Changes in Free Energy for the Isotherms

As was shown in our second paper [2], the value of the reduced equilibrium constant φ is calculated from the formula:

$$\varphi = \frac{k_c}{k_a} \qquad (2)$$

where k_c is the solubility product, and k_a is the activity product.

The change in the free energy ΔF, which is the energy characteristic deviation of the real equilibrium in the system from the ideal equilibrium determined by the law of mass action, is calculated from the formula:

$$\Delta F = -RT \ln \varphi \ , \qquad (3)$$

where T is the absolute temperature.

Using the nomenclature adopted in Table 1, we get the following computational formulas for the isotherms:

for reduced equilibrium constants:

$$\left.\begin{aligned} \bar{\varphi}_1 &= \frac{m^m L_1^{m+1}}{C_1(mC_1 + nC_2)^m} \\ \bar{\varphi}_2 &= \frac{n^n L_2^{n+1}}{C_2(mC_1 + nC_2)^n} \end{aligned}\right\} \ , \qquad (4)$$

for changes in the free energy:

$$\left.\begin{aligned} \Delta\bar{F}_1 &= -4.5787\ T \log \bar{\varphi}_1 \\ \Delta\bar{F}_2 &= -4.5787\ T \log \bar{\varphi}_2 \end{aligned}\right\} . \qquad (5)$$

It follows from Equation (4) that the magnitude of the reduced equilibrium constant $\bar{\varphi}$ for the isotherm T is a complicated function of the solution concentration, varying within the limits:

$$\left.\begin{aligned} L_1 > C_1 > \underline{l}_1 \\ 0 < C_2 < \underline{l}_2 \end{aligned}\right\} \ , \qquad (6)$$

for the first-component branch, and:

$$\left.\begin{aligned} L_2 > C_2 > \underline{l}_2 \\ 0 < C_1 < \underline{l}_1 \end{aligned}\right\} . \qquad (7)$$

for the second component branch.

For ideal equilibria, determined by the mass-action law, $\bar{\varphi} = 1$. On the other hand, the value of $\bar{\varphi}$ differs from unity for real equilibria.

4. Polythermal Change of Solubility With the Percentage of the Second Component Held Constant

According to the Schroeder-Le Chatelier equation, in a two-component system the individual solubility is an exponential function of the temperature:

$$L_1 = \exp\left(\frac{A_1}{T} + B_1\right) . \qquad (8)$$

If the solvent is changed, the coefficients A_1 and B_1 will have different values, but the nature of the function will remain unchanged.

Introducing a substance into the solvent will change the latter's properties, and hence an unsaturated solution with a constant concentration may be considered to be a new solvent.

Assume we have a solution consisting of a three-component system (1), which

is saturated with the first component, its concentration being C_1, but in which the concentration of the second component C_2 satisfies the following conditions within the temperature range under examination

$$\left.\begin{aligned} C_2 &< \underline{l}_2 \\ C_2 &= \text{constant} \end{aligned}\right\} . \tag{9}$$

Hence, as in the case of Equation (8), we may write:

$$C_1 = \exp\left(\frac{a_1}{T} + b_1\right) , \tag{10}$$

where a_1 and b_1 are constants.

Correspondingly, for solutions saturated with the second component, to which the conditions:

$$\left.\begin{aligned} C_1 &< \underline{l}_1 \\ C_1 &= \text{constant} \end{aligned}\right\} , \tag{11}$$

apply, we have:

$$C_2 = \exp\left(\frac{a_2}{T} + b_2\right) . \tag{12}$$

We select the NaCl – KCl – H_2O and NaCl – $MgCl_2$ – H_2O systems, which have been explored over a wide temperature range, as examples that bear out the correctness of Equations (10) and (12).

The solubility data for the NaCl – KCl – H_2O system [3] are listed in Tables 2 and 3 and illustrated in Figs. 1 and 2.

TABLE 2

Solubility of Sodium Chloride (C_1) in Aqueous Solutions Containing Potassium Chloride (C_2)
Grams per 1000 Grams of Water

t (°)	T °K	$\frac{1}{T}$	C_2 = 300		C_2 = 400	
			C_1	log C_1	C_1	log C_1
100	373	0.002681	280	2.4472	–	–
150	423	0.002364	333	2.5224	303	2.4814
200	473	0.002114	389	2.5899	364	2.5611
250	523	0.001912	437	2.6405	420	2.6232
300	573	0.001745	490	2.6902	472	2.6739

TABLE 3

Solubility of Potassium Chloride (C_2) in Aqueous Solutions Containing Sodium Chloride (C_1)
Grams per 1000 grams of water

t (°)	T °K	$\frac{1}{T}$	C_1 = 300		C_1 = 200	
			C_2	log C_2	C_2	log C_2
100	373	0.002681	480	2.6812	400	2.6021
150	423	0.002364	606	2.7825	533	2.7267
200	473	0.002114	743	2.8710	682	2.8338
250	523	0.001912	884	2.9465	826	2.9170
300	573	0.001745	1026	3.0111	966	2.9850

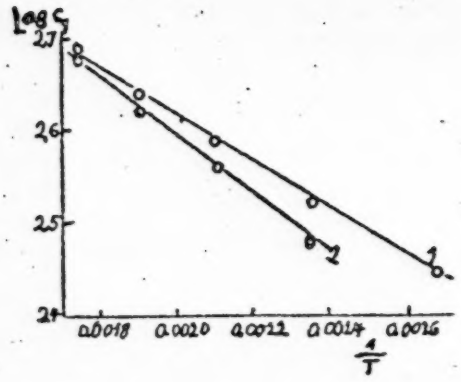

Fig. 1. Solubility of NaCl (C_1) in solutions containing KCl (C_2).

$1 - C_2 = 300$; $2 - C_2 = 400$.

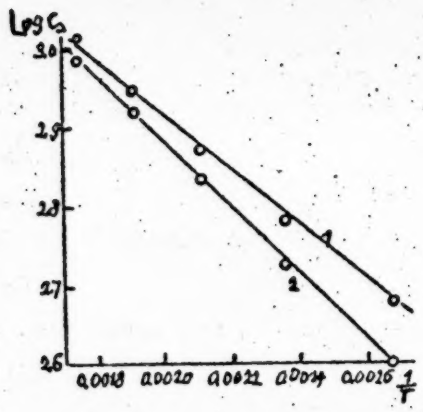

Fig. 2. Solubility of KCl (C_2) in solutions containing NaCl (C_1).

$1 - C_1 = 100$; $2 - C_1 = 200$.

In these graphs the reciprocals of the absolute temperature are plotted along the axis of abscissas, and the logarithms of the concentration of the component with which the solution is concentrated along the axis of ordinates.

The diagrams indicate that there is a linear relationship between the logarithms of concentration and the reciprocals of the absolute temperature over a wide temperature range, i.e., Equations (10) and (12) hold.

The solubility data for the $NaCl - MgCl_2 - H_2O$ system [3] are listed in Table 4 and plotted in Fig. 3. Only the sodium-chloride branch was taken, owing to the fact that the concentration of magnesium chloride practically coincides with the individual solubility at the eutonic point of the system.

TABLE 4

Solubility of Sodium Chloride (C_1) in Aqueous Solutions Containing Magnesium Chloride (C_2). Grams per 1000 grams of water.

t (°)	T °K	$\frac{1}{T}$	$C_2 = 100$		$C_2 = 300$		$C_2 = 500$	
			C_1	log C_1	C_1	log C_1	C_1	log C_1
100	373	0.002681	282	2.4502	106	2.0253	12	1.0792
125	398	0.002513	298	2.4742	120	2.0792	20	1.3010
150	423	0.002364	312	2.4942	138	2.1399	34	1.5315
175	448	0.002232	330	2.5185	156	2.1931	52	1.7160
200	473	0.002114	354	2.5490	176	2.2455	66	1.8195

We see from the diagram (Fig. 3) that Equation (10) holds for this case as well.

Evidently, this functional relationship may be applied to multicomponent systems.

5. Changes in the Reduced Equilibrium Constants and the Free Energy for Isotherms

As was shown in our second paper [2], the reduced equilibrium constant φ varies exponentially with temperature.

As applied to the equilibrium state in system (1), we may, for example, write:

$$\ln \bar{\varphi}_1 = \frac{A_{\varphi,1}}{T} + B_{\varphi,1} \qquad (13)$$

for the first component, where $A_{\varphi,1}$ and $B_{\varphi,2}$ are constants.

Eliminating the temperature T from equations (10) and (13) yields:

$$\ln \bar{\varphi}_1 = \bar{A}_{\varphi,1} + \bar{B}_{\varphi,1} \ln C_1, \qquad (14)$$

where $\bar{A}_{\varphi,1}$ and $\bar{B}_{\varphi,1}$ are constants.

For the second component we may write

$$\ln \bar{\varphi}_2 = \bar{A}_{\varphi,2} + \bar{B}_{\varphi,2} \ln C_2. \qquad (15)$$

similar to equation (14).

Equations (14) and (15), which are correct if Conditions (9) and (11) are observed, indicate that along an isotherm the logarithm of the reduced equilibrium constant is proportional to the logarithm of the concentration of the component with which the solution is saturated.

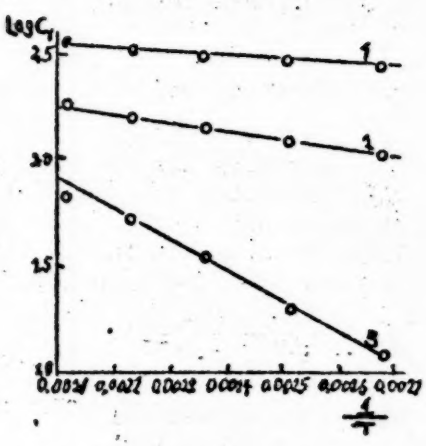

Fig. 3. Solubility of NaCl (C_1) in solutions containing $MgCl_2$ (C_2)

1-(C_2) = 100; 2-(C_2) = 300; 3-(C_2) = 500.

Combining Equations (3), (14), and (15), we get

$$\Delta\bar{F}_1 = (\bar{A}_{F,1} + \bar{B}_{F,1} \ln C_1)\, T; \qquad (16)$$

$$\Delta\bar{F}_2 = (\bar{A}_{F,2} + \bar{B}_{F,2} \ln C_2)\, T, \qquad (17)$$

where $\bar{A}_F$ and $\bar{B}_F$ are constants.

It follows from Equations (16) and (17) that along an isotherm the change in free energy is proportional to the logarithm of the concentration of the component with which the solution is saturated.

We give the data for the NaCl – KCl – H_2O and NaCl – $MgCl_2$ – H_2O systems as examples illustrating the correctness of Formulas (14) and (15) for changes in the reduced equilibrium constants along an isotherm and of Formulas (16) and (17) for changes in the free energy.

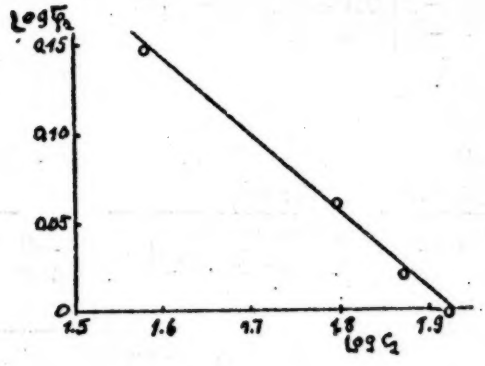

Fig. 4. NaCl – KCl – H_2O, 20° isotherm. KCl branch.

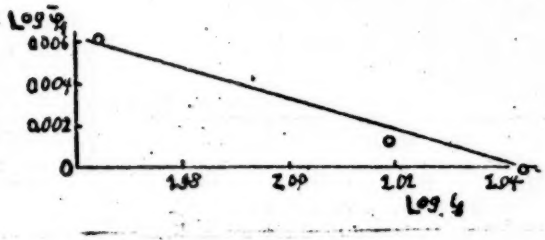

Fig. 5. NaCl – KCl – H_2O, 20° isotherm. NaCl branch.

The data for the NaCl – KCl – H_2O system [4] at the 20° isotherm are listed in Table 5 and plotted in Figs. 4 and 5. In the graphs the abscissas represent the logarithms of the concentration of the component with which the solution is concentrated, while the ordinates are the logarithms of the reduced equilibrium constant for the given component.

The diagrams show that the expected linear relationship actually exists. The sole exception is one point on the sodium-chloride branch (Table 5), corresponding to concentrations of $C_1 = 97.30$ and $C_2 = 31.36$ (Table 5). The value of the reduced constant at this point is lower than at adjacent points, and it may be assumed that the experimental data for this point are not accurate enough.

The data for the NaCl – $MgCl_2$ – H_2O system [4] at this 40° isotherm are cited in Table 6 and plotted in Fig. 6. Here too, we see that the correctness of Equations (14), (15), (16) and (17) is again confirmed. We do not reproduce the data for the magnesium chloride branch for the reason cited above.

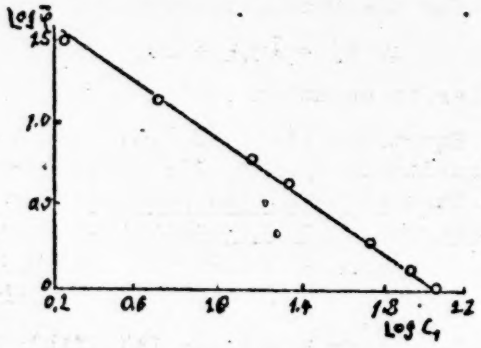

Fig. 6. NaCl – $MgCl_2$ – H_2O, 20° isotherm. NaCl branch.

TABLE 5

NaCl – KCl – H_2O

Data in Mols per 1000 Mols H_2O. 20° Isotherm

NaCl		KCl		Reduced equilibrium constant		log $\bar{\Phi}_1$	log $\bar{\Phi}_2$	Change in free energy		Solid phase
C_1	log C_1	C_2	log C_2	$\bar{\Phi}_1$	$\bar{\Phi}_2$			$-\Delta F_1$	$-\Delta F_2$	
110.38	2.0429	–	–	1	–	0	–	0	–	NaCl
104.00	2.0170	12.70	–	1.003	–	0.0013	–	1.744	–	NaCl
(97.30)	1.9881	(31.36)	–	0.9732	–	-0.0118	–	-15.83	–	NaCl
91.90	1.9633	38.16	1.5816	1.014	1.404	0.0060	0.1474	8.103	197.7	NaCl + KCl
34.32	–	62.46	1.7956	–	1.153	–	0.0618	–	82.95	KCl
14.62	–	74.44	1.8718	–	1.051	–	0.0216	–	28.97	KCl
–	–	83.48	1.9216	–	1	–	0	–	0	KCl

TABLE 6

NaCl – $MgCl_2$ – H_2O

Data in Mols per 1000 Mols H_2O. 40° isotherm

NaCl		$MgCl_2$	Reduced equilibrium constant	log $\bar{\Phi}_1$	Change in free energy	Solid phase
C_1	log C_1	C_2	$\bar{\Phi}_1$		$-\Delta\bar{F}_1$	
112.60	2.0515	0	1	0	0	NaCl
83.30	1.9207	16.92	1.299	0.1136	162.8	NaCl
53.36	1.7272	33.60	1.971	0.2947	423.3	NaCl
20.88	1.3197	60.16	4.301	0.6336	908.0	NaCl
14.26	1.1541	66.53	6.035	0.7807	1119	NaCl
5.04	0.7024	88.44	13.83	1.1408	2018	NaCl
1.80	0.2553	108.33	32.24	1.5084	2162	NaCl

SUMMARY

1. It has been shown that in a three-component system a solution that is unsaturated with respect to one component may be considered a new solvent with respect to the component with which the solution is saturated.

2. It has been shown that the change in solubility with temperature for the component saturating a solution that has a constant percentage of the other component follows an exponential law.

3. It is demonstrated that along an isotherm the logarithm of the reduced equilibrium constant is proportional to the logarithm of the concentration of the component with which the solution is saturated. Hence, along an isotherm, the change in the free energy is proportional to the logarithm of the concentration of the component with which the solution is saturated.

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Received November 28, 1947.

See CB translation p. 15 ff.

ENTROPY OF THE HYDRATED NICKEL ION

M. S. Barvinok

In a previous paper [1] we calculated the entropy of the hydrated bivalent cobalt ion, employing Thomsen's thermochemical measurements [2]. The considerations arising in our calculation of the entropy of the Co^{++} ion led us to determine the entropy of the nickel ion as well. The calculation of the entropy of Ni^{++} ion was done by the method used by Latimer and his associates [3] for aqueous solutions. It consists of computing ΔS, the entropy of the chemical reaction between the reacting substances M and X in an aqueous solution, which is obtained from the equation:

$$\Delta F = \Delta H - T\Delta S, \qquad (1)$$

which gives the change in the free energy of a chemical reaction, ΔF, as a function of the heat of reaction, ΔH, the entropy of the reaction, ΔS, and the absolute temperature T. All the values are for a standard state, chosen arbitrarily. The standard state used is the hypothetical molar solution. It is defined as the homopolar solution of ions that obey the law of a true dilute solution, with the ion heat content that they would have for infinite dilution [3,4].

For the standard state, Equation (1) is rewritten as follows:

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ,$$

where ΔF°, ΔH°, and ΔS° are the changes in the free energy, heat content, and entropy, respectively, referred to the standard state. All computations in the present paper have been made for T = 298.1° K. The ΔF° of the reaction is determined as the difference between the free energy of the reaction products (from their elements) and the free energy of the reagents. The free energy of all the elements and of the hydrogen ion is taken as zero in their standard state [5].

$$M + X = MX.$$

$$\Delta F^\circ = F^\circ_{MX} - \Delta F^\circ_M - \Delta F^\circ_X.$$

The change in the entropy of the reaction, ΔS°, is computed as the difference between the entropy of the reaction products and the entropy of the reagents in their standard state. The entropy of the hydrogen ion is taken equal to zero [3].

Calculation of the Entropy of the Hydrated Bivalent Ni^{++} Ion

(Based on Experimental Data)

The two following chemical reactions were employed for this calculation.

First Reaction:

$$NI_S + Br_2\ (l)aq = Ni^{++} + 2Br^-. \qquad (I)$$

Thomsen [2] measured the heat of this reaction for a dilute aqueous solution:

$$\Delta H = -71820 \text{ cal/m}.$$

1. Computation of ΔF for the first reaction:

$$\Delta F^\circ = \Delta F^\circ_{Ni^{++}} + 2\Delta F^\circ_{Br^-} - \Delta F^\circ_{Ni(S)} - \Delta F^\circ_{Br_2(l)aq},$$

$\Delta F^\circ_{Ni^{++}} = -11530$ cal/mol. [6],

$\Delta F^\circ_{Br^-} = -24578$ cal/mol. [5],

$\Delta F^\circ_{Br_2aq} = 977$ cal/mol [5],

$\Delta F^\circ = -11530 + 2(-24578) - 977 = -61663$ cal/mol.

2. Computation of ΔS° for the first reaction:

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ; \quad \Delta S^\circ = \frac{\Delta H - \Delta F^\circ_{Br_2(l)}}{T}$$

$$\Delta S^\circ = \frac{-71820 + 61663}{298.1} = -34.07 \text{ entropy units}$$

3. Computation of the entropy of Ni^{++} :

$$\Delta S^\circ = S^\circ_{Ni^{++}} + 2S^\circ_{Br^-} - S^\circ_{Ni(S)} - S^\circ_{Br_2(l)},$$

$\Delta S^\circ_{Br^-} = 19.7$ [7] entropy units,

$\Delta S^\circ_{Ni(S)} = 7.1$ [6] entropy units,

$\Delta S^\circ_{Br_2(l)} = 36.8$ [6] entropy units,

$S^\circ_{Ni^{++}} = -34.07 - 2 \cdot 19.7 + 7.1 + 36.8 = -29.57 \sim -29.6$ e.u.

Second Reaction:

$$Ni_{(S)} + Cl_2(g)aq = Ni^{++} + 2Cl^-, \quad \Delta H = -94230 \text{ [8] cal/mol., (II)}$$

4. Computation of ΔF° for the second reaction:

$\Delta F^\circ_{Ni^{++}} = -11530$ cal/mol.

$\Delta F^\circ_{Cl_2(g)aq} = 1630$ cal/mol.

$\Delta F^\circ_{Cl^-} = -31330$ cal/mol.,

$\Delta F^\circ = -11530 + 2(-31330) - 1630 = -75820$ cal/mole.

5. Computation of ΔS° for the second reaction.

It follows from the data of Bichowsky and Rossini that $\Delta H = -942.30$ refers to $NiCl_2$ diluted in 800 mols of water and differs but slightly from ΔH°. Hence:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T} = \frac{-94230 + 75820}{298.1} = -61.76 \text{ entropy units.}$$

6. Computation of the entropy of the hydrated Ni^{++} ion:

$$\Delta S^\circ = S^\circ_{Ni^{++}} + 2S^\circ_{Cl^-} - S^\circ_{Ni(S)} - S^\circ_{Cl_2(g)},$$

$S^\circ_{Cl_2(g)} = 52.6$ [8] entropy units.

$S^\circ_{Cl^-} = 13.5$ [8] entropy units;

$S^\circ_{Ni^{++}} = 61.8 - 27 + 7.1 + 52.6 = -29.1$ entropy units.

If it is remembered that the accuracy of the known values of the entropy of

hydrated ions is of the order of one entropy unit, the coincidence of the two values for the entropy of the hydrated Ni^{++} ion obtained with the foregoing reactions is quite satisfactory.

A.F.Kapustinsky [10] calculated the entropy of the nickel ion from the Goldschmidt radii, finding $S^{\circ}_{Ni^{++}} = -31$ entropy units. In view of the precision of measurement of ion entropy, it may be said that the values we have found for $S^{\circ}_{Ni^{++}}$ from the chemical equations I and II lie close to the value derived by A.F. Kapustinsky from the Goldschmidt radii.

SUMMARY

1. The entropy of the hydrated bivalent nickel ion has been computed from the thermochemical data for two chemical reactions. The values obtained are 29.6 and 29.1 entropy units.

2. The value of $S^{\circ}_{Ni^{++}}$ obtained is close to that calculated by A.F.Kapustinsky from the Goldschmidt radii: (− 31 entropy units)

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Received January 16, 1948

THE RELATIONSHIP BETWEEN VISCOSITY AND CONDUCTANCE IN SOME BINARY MELTS OF SALTS

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E.Y.Gorenbein [1] measured the conductance, viscosity, and specific gravity of the $SbBr_3 - AlBr_3$, $ZnBr_2 - AlBr_3$, and $KBr - AlBr_3$ systems in the melted state, coming to certain conclusions, which we shall comment upon.

E.Y. Gorenbein writes: "The conductance curves corrected for molecular conductance look alike for all three systems, in which the coordination compounds $SbBr_3 \cdot AlBr_3$, $ZnBr_2 \cdot Al_2Br_6$, and $KBr \cdot Al_2Br_6$ were the electrolytes." We shall take up the justification for this correction later on. Here we shall merely note the following: the $SbBr_3 - AlBr_3$ system has been investigated throughout a wide range of concentrations, whereas the other two have been explored only up to 33-35 molecular per cent of $ZnBr_2$ or KBr, respectively. This circumstance alone does not justify our speaking of the identical nature of the curves. In the accompanying drawing (Fig. 1), we have plotted the curves showing the variation of μ' (the corrected molecular conductance) with φ (the dilution) for the above three systems at 100, 110 and 100°, respectively (the curves are taken from Figs. 4, 9, and 11 of the cited paper by Gorenbein). The curve for the first system has a maximum approximately corresponding to the dilution at which the quantities of $SbBr_3$ and $AlBr_3$ are equimolecular, i.e., they correspond to the coordination compound $SbBr_3 \cdot AlBr_3$. The curve for the second system rises monotonously; the curve for the third system rises monotonously, but its curvature is opposite in sign to that of the second curve. Thus there is hardly any reason to speak of the identical nature of the curves. What is common to these curves is the fact that they all rise with increasing concentration of the dissolved salt up to a dilution that corresponds approximately to the composition of the coordination compounds formed in the solutions, i.e., $SbBr_3 \cdot AlBr_3$, $ZnBr_2 \cdot AlBr_3$, and $KBr \cdot Al_2Br_6$. The rising trend of such curves is always found in systems with increasing viscosity, however.

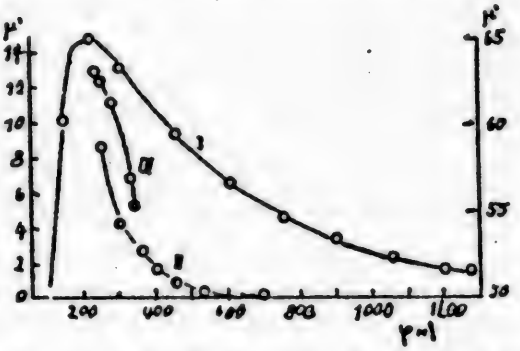

Fig. 1. I – the $SbBr_3 - AlBr_3$ system; II – the $ZnBr_2 - AlBr_2$ system; III – the $KBr - AlBr_3$ system; The scale of ordinates μ' at the left applies to Curves I and II; the scale of ordinates μ' at the right applies to Curve III.

We do not know the reasons that led Gorenbein to explore the solutions of $ZnBr_2$ and KBr in aluminum bromide only up to 33-35 mol %, but we must state that the results obtained by this author do not justify his assertion in his conclusions that "the highest corrected molecular conductance corresponds to the conductance of the foregoing electrolytes," i.e., $SbBr_3 \cdot AlBr_3$; $ZnBr_2 \cdot Al_2Br_6$ and $KBr \cdot Al_2Br_6$. The meaning that Gorenbein attaches to the word "corresponds" is unclear. If Gorenbein had in mind the correspondence of the maximum on the $\mu' - \varphi$ curve to the stoichiometrical ratio between the system components, this assertion is approximately correct

for the $SbBr_3$ – $AlBr_3$ system, in which the maximum occurs at 46.5 mol.% of $SbBr_3$. This can hardly be said of the two other systems, since the "highest" values of μ' cannot be assigned to maxima, of whose existence and position nothing is known. Corresponding experiments at higher electrolyte concentrations are required. The "highest" values of μ' are by no means the highest possible values, but the highest values found by Gorenbein in an inadequate concentration range. To judge from the shape of the curves, the highest values of μ' won't correspond at all to the $ZnBr_2$:$2AlBr_3$ and KBr:$2AlBr_3$ ratios, unless we make the highly improbable assumption that the curves will have sharp maxima at the stated points.

In his conclusions, Gorenbein also states: " The shape of the curves of corrected molecular conductance bears out my assertion that every dissolved substance tends to assume a state, as the concentration is raised, that is characteristic of it in melt, and that the highest corrected molecular conductance corresponds to the corrected conductance existing in a solution of the electrolyte in the melted state." (Also cf p. 738 in the same article [1].) This assertion, which was called a hypothesis [2] earlier (1940) is not supported by the factual material in the paper, nor in Gorenbein's previous papers [2,3] which we mentioned at an earlier date [4]. Let us consider the data in this paper [1]. Gorenbein states that in these systems the coordination compounds $SbBr_3 \cdot AlBr_3$, $ZnBr_2 \cdot Al_2Br_6$, and $KBr \cdot Al_2Br_6$ are formed. Hence, in this case the dissolved substances ($SbBr_3$, $ZnBr_2$ and KBr) will combine with the aluminum bromide to form coordination compounds. These compounds do not at all "tend to assume a state that is characteristic of it in a melt", since their melting points lie below the temperatures of the experiments. In fact, the $SbBr_3$ – $AlBr_3$ system was investigated at 100, 110, 120, 130, and 140°, while the melting point of $SbBr_3 \cdot AlBr_3$ is 85.2°; the $ZnBr_2$ – $AlBr_3$ system was investigated at 110, 120, 130, 140, and 150°, while the melting point of $ZnBr_2 \cdot Al_2Br_6$ is 111.5°; and the KBr – $AlBr_3$ system was investigated at 100°, while the melting point of $KBr \cdot Al_2Br_6$ is 95.8° [5]. As we see, in only one of the 11 series of measurements was the melting point of the complex salt higher than the experimental temperature (1.5° in all). Thus, the shape of the curves of corrected molecular conductance can in no way support Gorenbein's quoted assertion.

Moreover, we do not know what is the correspondence between the "highest corrected molecular conductance" (of a salt dissolved in aluminum bromide) and the "corrected conductance of the electrolyte formed in the solution."

Let us examine the most fundamental passages in the evaluation of the literature and experimental data in Gorenbein's article [1]. On Page 730, Gorenbein writes: "When the system consists, not of two components, but – as we saw in the unstable systems – of three, the variation of the conductance with viscosity is more complex and may be expressed by the equation $\mu \cdot \eta^m = \text{const.}$" This assertion is completely untrue. It suffices to point out that K.S.Yevstropyev [6], developing Johnston's old research [7], demonstrated the correctness of the cited equation for aqueous solutions of such typical strong electrolytes as KNO_3, NaCl, and $BaCl_2$, i.e., for ordinary binary systems.

In Gorenbein's assertion that the simple viscosity correction applied by him to the conductance is admissible for binary systems, nothing is said about the concentrations at which this correction is applicable. (The correction is made in accordance with the equation $\mu' = \mu \frac{\eta}{\eta_0}$, where η is the solution viscosity and η_0 is the solvent viscosity). Gatchek, [8] cites considerable data which support the general assertion that this correction can be applied reliably only to dilute solutions whose viscosity does not differ much from that of the solvent. A.I. Rabinowitsch [9,10] noted that strict observance of inverse proportionality between μ and η is hardly possible throughout a wide dilution range. In this connection Gorenbein says that in his previous researches [1,2,3] he championed the point of

view that in systems in which there are more molecules of the electrolyte than of the solvent and the system remains a binary one... the viscosity is inversely proportional to the conductance" and earlier, on p. 729, Gorenbein says: "In the binary systems (electrolyte and nonelectrolyte) in which the molecules of the solute are considerably more numerous than the molecules of the solvent, it may be assumed that the viscosity and the molecular conductance are inversely proportional to each other." Gorenbein furnished no proof whatsoever of this inverse proportionality in the objects he investigated, confining himself to the uniform and unrestricted application of a correction to all cases at all concentrations. This approach cannot be accepted as correct as a matter of principle. A.I. Rabinowitsch employed a simple viscosity correction for concentrated aqueous solutions of a number of salts, but he stressed the conditional nature of this approach, which results in exaggerated figures, by placing the word "corrected" conductance in quotation marks: "korrigierte" 9, and calling the method he used "over correction" ("Uberkorrektion") [9,10].

This approach enabled Rabinowitsch, however, to prove the applicability to aqueous solutions of the well-known Walden equation [11] for the location of the minimum on the conductance curve according to the formula: $V_{min} \cdot \varepsilon^3 = \text{const.}$, where V is the dilution, and ε is the dielectric constant of the solvent.

In order to establish the applicability of a simple viscosity correction to conductance we employed a simple method, consisting of the following: plotting diagrams of the logarithms of molecular conductance and viscosity as functions of composition, expressed in molecular per cent. If the viscosity were inversely proportional to the molecular conductance, $\log \mu\eta = \text{constant}$, and, hence, the variable $\log \mu\eta$ would be a straight line parallel to the axis of abscissas. The $\log \mu\eta$ - composition curve can be plotted by adding the ordinates of $\log \mu$ and $\log \eta$ for each composition.

The curves of $\log \mu\eta$ -composition in the given binary systems may be plotted with a certain degree of approximation by measurements taken from the corresponding diagrams in Gorenbein's article, since the article does not provide the necessary numerical data, with the exception of data for μ and η in the $KBr - AlBr_3$ system.

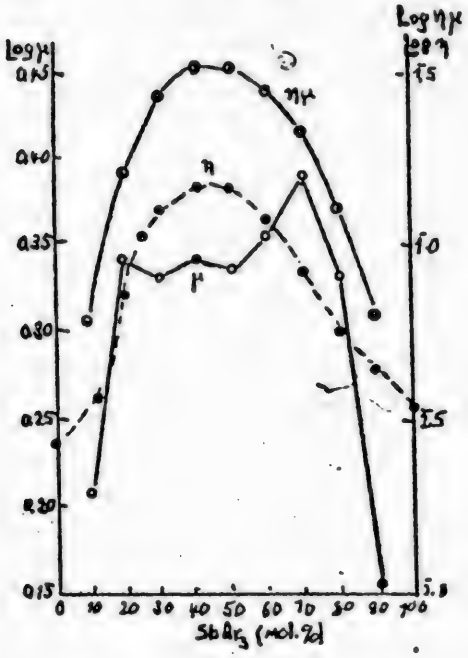

Fig. 2

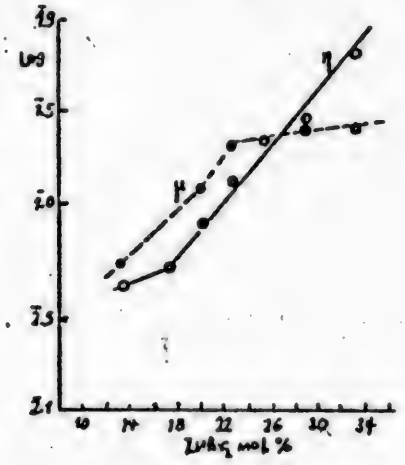

Fig. 3.

Figures 2, 3, and 4 are diagrams showing the variation of log μ and log η with the composition for the following systems: $SbBr_3 - AlBr_3$; $ZnBr_2 - AlBr_3$; and $KBr - AlBr_3$, respectively. As we see, the logarithmic plot does not exhibit correspondence between the viscosity and the conductance in a single case. The relationships between these properties are complex and various. The variation of log $\mu\eta$ with composition is shown in Figs. 2 and 4. As we see, the curves are not parallel to the composition axis, which means that there is no inverse proportionality between viscosity and conductance. Hence, there is no justification for applying a simple viscosity correction as Gorenbein has done. We have not plotted the function log $\mu\eta$ -composition in Fig. 3 because it is evidently unnecessary to do so. We may merely add that Figs. 3 and 4 clearly exhibit a straight-line variation of the conductance and viscosity with composition. In Yevstropyev's papers [6,12, 13] such relationships were found to exist for a number of binary melts of salts. But in the cases we are discussing these relationships are of a more complex nature than in Yevstropyev's examples, which indicates the presence of various chemical interactions in the systems investigated by Gorenbein.

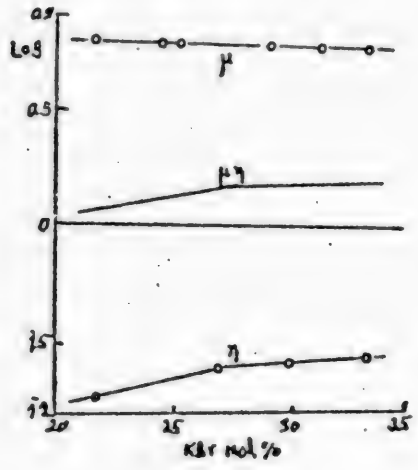

Fig. 4.

From the above, we are able to determine conclusively that the work of Gorenbein [1], applying a series of simple corrections for viscosity to conductance, is not only confused, but has no base.

SUMMARY

1. The experimental data of E.Y.Gorenbein on the viscosity and conductance of the fused systems: $SbBr_3 - AlBr_3$, $ZnBr_2 - AlBr_3$, and $KBr - AlBr_3$ have been subjected to analysis.

2. The problem of the permissibility of applying a simple viscosity correction to the molecular conductance in accordance with the expression $\mu' = \mu \cdot \frac{\eta}{\eta_0}$, where η is the viscosity of the solution, and η_0 is the viscosity of the solvent, has been examined. It has been shown that this correction is inapplicable to the systems mentioned.

3. The groundlessness of E.Y.Gorenbein's conclusions concerning the applicability of a simple viscosity correction to molecular conductance has been proved.

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Received April 4, 1947.

A NOTE ON THE COMMENTS OF D. A. POSPEKHOV "THE RELATIONSHIP BETWEEN VISCOSITY AND CONDUCTANCE IN SOME BINARY MELTS OF SALTS"

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Let us consider D. Pospekhov's basic assertions.

1. Pospekhov takes exception to my statement regarding the identical nature of the $\mu_1 - \varphi$ (μ_1 is the corrected molecular conductance, and φ is the dilution). The molecular conductance, corrected for viscosity, is of an anomalous nature as dilution proceeds; as was shown graphically in our paper. This is what is common to the course of the $\mu_1 - \Phi$ curves. It seems to me that any chemist understanding the essential nature of anomalous molecular conductance would hardly make an objection of this sort.

2. It is stated in these comments that no reason is known which led me to investigate solutions of $ZnBr_2$ and KBr in $AlBr_3$ as the solvent only up to component ratios corresponding to the composition of the coordination compounds, the presence of which was established by thermal analysis, [1].

In our paper, which Pospekhov endeavors to criticize, the reasons that led us to investigate the $ZnBr_2 - AlBr_3$ and $KBr - AlBr_3$ systems within the stated concentration range (from pure $AlBr_3$ to the ratios $ZnBr_2:Al_2Br_6$ and $KBr:Al_2Br_6$) are quite clearly stated on Pages 735 and 738.

In this series of papers [2] we asserted more than once that we are investigating binary systems of an electrolyte and a nonelectrolyte. In the systems we investigated, the electrolytes were coordination compounds of aluminum bromide. If the concentrations of the salts $ZnBr_2$ or KBr in these systems were increased beyond the ratios corresponding to the compositions of the coordination compounds $ZnBr_2 \cdot Al_2Br_6$ and $KBr \cdot Al_2Br_6$, we might have gotten a mixture of electrolytes: $ZnBr_2 \cdot Al_2Br_6 + ZnBr_2$ in the first system, and $KBr \cdot Al_2Br_6$, $KBr \cdot AlBr_3$ and KBr in the second system, according to the data of thermal analysis, which would have contradicted the object of our research.

The highest corrected molecular conductance (cf the graphs of the criticized papers*) corresponds to this composition of the coordination compounds: $ZnBr_2 \cdot Al_2Br_6$, $KBr \cdot Al_2Br_6$, and $SbBr_3 \cdot AlBr_3$.

3. Then D.A.Pospekhov asserts that "these compounds do not at all" tend to attain the state that they possess in the melted state, "since their melting points lie above the temperature of the experiments."

Here, D.A.Pospekhov has failed to understand the point at issue.

In making a comparison between the molecular state of an electrolyte in its individual liquid state and in concentrated solutions, we stated that every dissolved substance strives to attain a state in which it would be liquid (melted). In

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*A detailed paper, containing numerical data, was submitted to the periodical Zapiski of the Institute of Chemistry of the USSR academy of Sciences in 1941, but was lost during the war.

other words, as the concentration rises, the regularity of the solution also increases, the maximum regularity of the solution at a given temperature corresponding to the ultimate electrolyte concentration, i.e., the individual liquid state. This state corresponds to the highest corrected molecular conductance at the given temperature, which was established experimentally [2].

Let us consider the isotherms of the $\mu_1 - \varphi$ curves as the electrolyte concentration is raised continuously. Naturally, the highest regularity of the electrolyte will be found to exist when we reach the ultimate concentration, i.e., its individual liquid state at the temperature of the investigation. The state of fusion must not be confused with the melted state, as at any given temperature the melted state will be higher than the melting point (except in the supercooled state).

4. D.A.Pospekhov, considering the variation of μ with η, in his haste even proposed a "simple" method of "establishing the feasibility of applying a simple viscosity correction to the conductance."

This method is described in Pospekhov's remarks. We ask permission to make the following comments thereon.

a) In the literature with which we are familiar no one has ever asserted that the $\mu \cdot \eta$ product will be constant as the electrolyte concentration is changed. Even textbooks state that the $\mu \cdot \eta$ product will remain constant provided α = constant [4] (α is the degree of electrolytic dissociation) over a small temperature range.

Inasmuch as the $\mu \cdot \eta$ product is not a constant as the component ratio in the systems changes, neither will the log $\mu \cdot \eta$ be constant as the concentration varies. Where Pospekhov got that idea I do not know.

b) D.A.Pospekhov is looking for constancy of log $\mu \cdot \eta$ as the composition of the system changes, using our experimental data for that purpose. Fascinated by his "simple" method, the author evidently failed to notice that our very data indicated that the $\mu \cdot \eta$ product changes as the composition changes. Moreover, we are exploring the change in $\mu \cdot \eta$ with a change in concentration (cf the $\mu_1 - \varphi$ curves in the criticized paper) and are drawing the corresponding conclusions therefrom.

c) We can reach a more or less well-founded idea of the variation of μ with η from the temperature coefficients of conductance and viscosity at a constant electrolyte concentration.

That is exactly what we did in considering the variation of μ with η (cf Pospekhov's references to our paper).

D.A.Pospkehov's references to the paper by K.S.Yevstropyev serve to mislead the reader.

K.S.Yevstropyev [5] quite correctly considers the change in the $\lambda \cdot \eta$ product with changes of temperature at a given constant electrolyte concentration. This method has nothing in common with the "simple" method of our critic.

Yevstropyev's data do not contradict the feasibility of applying a simple viscosity correction in accordance with the formula $\mu_1 = \mu \cdot \frac{\eta_p}{\eta_o}$. This enables him to reduce the conductance to the viscosity of the pure solvent. In introducing viscosity corrections according to the formula $\mu_1 = \mu \cdot \left(\frac{\eta_p}{\eta_o}\right)^m$, we introduce the empirical constant "m" which is close to unity when considering the

constancy of $\lambda \cdot \eta^m$ = constant as the temperature changes with constant concentration.

We discussed existing viewpoints on the problem of the effect of viscosity upon conductance as long ago as 1940 [6].

In all our research on concentrated electrolytic solutions, we have been examining the change in the corrected molecular conductance with dilution [2] in various media.

Suppose we were to introduce a viscosity correction based on the formula $\mu_1 = \mu \cdot \left(\frac{\eta_p}{\eta_o}\right)^m$, which Pospekhov defends. What difference would that make in μ_1 as a function of φ? For the nature of the $\mu_1 - \varphi$ curves would remain the same (anomalous shape). We would merely complicate the work of computation.

It is somewhat strange that D.A.Pospekhov, while criticizing our work, does not touch upon similar papers by other authors, who introduced a viscosity correction long before I did, using the same procedure.

In conclusion, I must point out the following:

It is known that maxima, minima, or points of inflection on composition – property curves stand out better when the numerical data are not plotted on the system's coordinate axes in logarithmic form.

D. A. Pospekhov plots curves using the experimental data of other authors in logarithmic form.

The question involuntarily arises: what is the scientific value of this sort of work?

At bottom, if the curves reproduced in our paper, criticized by Pospekhov, which are not plotted logarithmically, and the same curves plotted by Pospekhov in logarithmic form are examined, we find no essential difference between them. It merely blurs the scattering of the points used to plot the curves and diminishes the prominence of whatever changes occur along the curves.

D.A.Pospekhov has contributed nothing new, and hence his "critical" comments are valueless and of no use to us.

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Received November 10, 1948.

THE SOLUBILITY OF DIPHENYLAMINE IN WATER

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The available data on the solubility of diphenylamine in water at temperatures adjacent to room temperature are quite contradictory.

Dehm [1] determined the solubility of diphenylamine in water in the temperature range of 20-25° by the gravimetric method, finding it to be 300 mg per 100 g of water ($1.77 \cdot 10^{-3}$ mol per 1000 g). But the author himself judges that his method is not very accurate.

According to Thiel [2], who used the colorimetric method, the solubility of diphenylamine at 15° is $1.87 \cdot 10^{-4}$ mol per liter (31.62 mg per liter).

In a paper on the methods for the colorimetric determination of small quantities of diphenylamine, Ponomarenko [3] states, without citing his source, that the solubility of diphenylamine in water is about 0.06 g per liter, which is nearly twice the value given by Thiel. The figure given in the text of the article, is 0.06 mg per liter, which is no doubt a slip of the pen or a typographical error.

Engaged in a study of diphenylamine as a solvent for use in an investigation of surface activity in nonaqueous solutions [4], we determined the solubility of this substance in water by means of a Zeiss interferometer with a chamber 3 cm long. A preparation marked "for analytical use" was employed in the experiments.

We first determined the value of the interferometer-drum divisions by means of readings taken with solutions of known concentration. These solutions were prepared as follows. A minute crystal of diphenylamine was weighed in a Vollmer microbalance. The weighed crystal was transferred to a 500-ml measuring flask. The solutions were prepared and measured at 20° temperature. The flask employed in preparing the solutions, the apparatus described below for studying solubility, the stirrer, and the sampling tube were all made of Jena glass. The double distilled water used in preparing the solutions and in the experiments was kept in paraffin-lined bottles. The results of the calibration of three solutions of known concentration are listed in Table 1. Table 1 shows that the value of a division on the drum of the interferometer averages $9.0 \cdot 10^{-6}$ mol per liter for the three solutions investigated.

To attain equilibrium, two opposite series of tests were made. Part of the tests were made in a flask fitted with a stirrer and a mercury seal, as specified by Andreyev [5]. The samples were taken by means of two tubes bent at right angles, passed through the stopper of the apparatus and a rubber bulb.

The second series of tests, which was much more comprehensive, was made directly in the chamber of the interferometer. The solution containing an excess of diphenylamine was heated to 100° and kept at that temperature for two to three hours. Then the solution was slowly cooled, and when its temperature had fallen to 35°, part of the solution together with a small amount of the suspended powder was transferred to the interferometer chamber, the thermostat-controlled water of which was likewise at 35°. The interferometer housing was well insulated against

heat loss. It took about 10 hours for the temperature to drop from 35° to 10°.

TABLE 1
Graduating the Interferometer

Solution No.	Concentration, mg per liter	Number of interferometer graduations	Value of one graduation, mol/l·10^{-6}
1	5.32	3.5	8.997
2	2.64	5.0	9.036
3	9.11	6.0	8.971

TABLE 2
Solubility of Diphenylamine in Water

Temperature, °	Number of interferometer graduations	Solubility, mol/l·10^{-4}
10	11.8	1.06
15	15.0	1.35
20	19.0	1.71
25	23.4	2.11
30	29.0	2.61

To ascertain the effect of possible contamination of the preparation upon the latter's solubility, experiments with the same weighed portion of powder were repeated several times. The preparation proved to be quite pure, as repeated washing did not change the solubility value. The two series of tests yielded identical values: the mean values are listed in Table 2.

It follows from Table 2 that the solubility determined by us is closest to the figure given by Thiel. Thus, at 15° the solubility as found by us is $1.35 \cdot 10^{-4}$ mol per liter, whereas the value found by Thiel for 15° coincided with our value for 20°. The figures given by other authors are much higher.

The data obtained by us are described by the equation:

$$\log c = a - \frac{b}{T},$$

where c is the solubility in mols per liter, T is the absolute temperature, a is 1.5786, and b is 1571.

SUMMARY

The solubility of diphenylamine in water has been measured by means of an interferometer.

The results obtained are described by the equation:

$$\log c = a - \frac{b}{T}.$$

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Received February 16, 1948.

THE REACTION BETWEEN IONS OF ALUMINUM AND FLUORINE

INVESTIGATION OF THE $Al(NO_3)_3$ - NaF - $Fe(NO_3)_3$ - KSCN SYSTEM IN A NITRIC-ACID SOLUTION

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Notwithstanding the existence of a large number of aluminum-fluoride coordination compounds, up to the present we possess no quantitative data, even of an approximate nature, concerning the binding energy between aluminum and fluorine in complex ions (in solutions).

The sole indications in the literature deal only with the relative stability of some fluorine coordination compounds with fluorine coordination compounds of aluminum.

Thus V.M.Tarayan [1], in a potentiometric determination of beryllium by titration with sodium fluoride, found that the stability of the aluminum (Na_3AlF_6) and beryllium (Na_2BeF_4) coordination compounds is nearly identical.

The statement is made in the same paper that the stability of the fluorine coordination compound of magnesium is considerably lower than that of the beryllium, and hence of the aluminum compound.

It follows from the paper by Köhl [2] that aluminum-fluorine coordination compounds are more stable than those of iron-fluorine, as the $Al^{\cdot\cdot\cdot}$ ion drives the $Fe^{\cdot\cdot\cdot}$ ion out of a double salt of iron fluoride and sodium fluoride.

This led I.V.Tanayev and M.I.Levina [3] to work out a titrometric determination of aluminum, using sodium fluoride, in the presence of iron thiocyanate, as an indicator.

In determining the instability constant of the simplest aluminum-fluorine complex ion, $AlF^{\cdot\cdot}$, we discovered two singular irregularities, which are reported herein.

We conducted this investigation photometrically by measuring the color intensity of solutions containing constant concentrations of $Fe(NO_3)_3$, KSCN, and NaF and varying concentrations of $Al(NO_3)_3$.

Determination of the instability constant by means of the investigation of such fairly complicated systems became feasible after the instability constants of the following complex ions: iron (III)-thiocyanogen, $Fe(SCN)^{\cdot\cdot}$, and iron-fluorine, $FeF^{\cdot\cdot}$, had been determined in previous research done in the analytical-chemistry laboratory of the Institute of General and Inorganic Chemistry of the Ukrainian Academy of Sciences [4,5].

These constants proved to be $4\cdot10^{-3}$ and $5\cdot10^{-6}$, respectively.

This quite appreciable difference in the stability of the foregoing complex ions explains the well-known decolorizing action of fluorides upon a colored ferric thiocyanate solution.

It also explains the considerable sensitivity of the colorimetric determination

of small quantities of fluorides by the ferric thiocyanate method.

It was likewise found that the optimum conditions were such that the concentration of thiocyanogen ions is about 1000 times that of the fluorine ions [6]. This corresponds to the ratio of the stabilities of the thiocyanogen and fluorine complex ions of iron.

When an aluminum salt is introduced into a solution containing $Fe(NO_3)_3$, KSCN, NaF, and their reaction products, some of the fluorine is combined into colorless aluminum-fluorine complex ions. This diminishes the concentration of the iron-fluorine complex ions and increases the concentration of the colored iron -thiocyanogen complex ions. Hence, the intensification of the solution's color, which is a measure of the formation of a coordination compound of the aluminum and fluorine ions, may be employed in studying the reaction $mAl^{\cdots} + nF' \rightleftarrows Al_mF_n^{3m-n}$.

In the course of our research it was found that the velocity of this reaction is rather low. Moreover, it turned out that when no fluorine was present, the intensity of the color of the iron-thiocyanate solution is noticeably weakened by aluminate nitrate (at the low concentration of potassium cyanate indicated below).

As a low velocity of the reaction between the ions is not too common a phenomenon, generally speaking, every new instance in this field is of general interest.

Some indications of the low velocity of the reaction between aluminum and fluorine ions may be gathered from the paper by Kurtenacker and Jurenka on the analytical determination of fluorine ions [7].

These authors recommend that titration of a saturated sodium-chloride solution of sodium fluoride be done with aluminum chloride at a temperature of 70-80°. The reaction is slow at room temperature.

Materials and Techniques

The preparations of $Fe(NO_3)_3$, KSCN, and NaF were purified, and their solutions in 0.1 N nitric acid were prepared and set aside as described previously [5].

The solution of aluminum nitrate in 0.1 N nitric acid was prepared with a "chemically pure" preparation. The molarity of the initial (0.1 mol) solution was determined gravimetrically (against Al_2O_3).

Solutions at other concentrations were prepared by diluting the initial 0.1 N solution with a solution of nitric acid.

The experiment consisted of the measurement and comparison of the optical densities of solutions containing nothing but $Fe(NO_3)_3$ and KSCN with those containing $Al(NO_3)_3$ and NaF as well.

The photocolorimeter (with diaphragm compensation) and the experimental technique have been described previously [5]. A green light filter was used.

Effect of Aluminum Nitrate Upon the Color of an Iron-Thiocyanogen Solution

This effect was explored in a series of solutions, all containing constant concentrations of $Fe(NO_3)_3$ ($0.204 \cdot 10^{-3}$ mol per liter), KSCN ($0.975 \cdot 10^{-3}$ mol/liter) and HNO_3 (0.1 N). The concentration of the complex iron-thiocyanogen ions, $Fe(SCN)^{\cdot\cdot}$, thus formed [with no $Al(NO_3)_3$ present] is $0.039 \cdot 10^{-3}$ mol per liter.*

*The concentration of $Fe(SCN)^{\cdot\cdot}$ ions can be readily computed from the equation $\frac{([Fe(NO_3)_3] - x)([KSCN] - x)}{x} = k$ where k is the instability constant of $Fe(SCN)^{\cdot\cdot}$, equalling $4 \cdot 10^{-3}$, and x is the concentration of $Fe(SCN)^{\cdot\cdot}$ ions.

The concentration of $Al(NO_3)_3$ was measured throughout a wide range – from $0.08 \cdot 10^{-3}$ to $8.60 \cdot 10^{-3}$ mol per liter, i.e., a ratio of 1:1000.

The solutions were prepared as follows. A series of solutions was prepared containing the same quantity of $Fe(NO_3)_3$ and varying quantities of $Al(NO_3)_3$. Just before measuring the optical density, potassium thiocyanate was added to the test solution.

As we have stated above, the acidity of the solutions was kept constant at 0.1 mol of HNO_3.

The optical data are listed in Table 1 and shown graphically in Fig. 1.

TABLE 1

Test No.	$Al(NO_3)_3$ concentration in millimoles per liter	log I_0/I	Relative intensity of solution color, %.
I	II	III	IV
1	–	0.3098	100
2	2.04	0.3054	98.58
3	4.08	0.2993	96.62
4	6.12	0.2933	94.68
5	8.16	0.2907	93.87
6	20.40	0.2708	87.41
7	40.80	0.2434	78.57
8	61.20	0.2262	73.02
9	81.60	0.2143	69.17

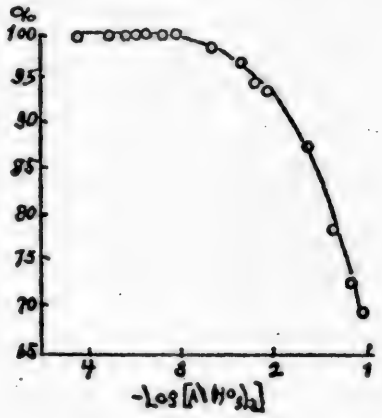

Fig. 1

The optical densities of the solution, (log I_0/I), is given in Col. III, the ratio of the optical densities of the test solutinns to that of a solution containing no $Al(NO_3)_3$, times 100, being given in Col. IV. Thus, the figures in Col. IV indicate the percentage ratio of the $Fe(SCN)^{\cdot\cdot}$ concentration in each solution containing $Al(NO_3)_3$ to the concentration of $Fe(SCN)^{\cdot\cdot}$ (100%) in the solution containing no $Al(NO_3)_3$.

In Fig. 1 the $Al(NO_3)_3$ concentration is shown as the negative logarithm ($-\log [Al(NO_3)_3]$) for convenience of reproduction.

As is shown by the curve in Fig. 1, the bleaching action of $Al(NO_3)_3$ upon the color of the iron-thiocyanogen solution is extremely slight, lying within the limits of experimental error for $Al(NO_3)_3$ concentrations up to $1 \cdot 10^{-3}$ mol per liter ($-\log [Al(NO_3)_3] > 3$).

But this effect increases at higher concentrations, becoming quite considerable at $Al(NO_3)_3$ concentrations of the order of 0.01 – 0.1 mol per liter.

All the figures listed in the table were obtained at comparatively low molar concentrations of $Fe(NO_3)_3$ and KSCN.

It may be supposed that the bleaching action of $Al(NO_3)_3$ will be less intensive if the $[Al(NO_3)_3] / [Fe(NO_3)_3]$ ratio is diminished.

In fact, the data of the table and Fig. 1 may be used to show that when the $[Al(NO_3)_3] / [Fe(NO_3)_3]$ ratio is less than 10, the intensity of the color of the $Fe(SCN)^{\cdot\cdot}$ solution is hardly weakened at all, whereas the bleaching is much greater at higher ratios (Experiments 4-9).

On the other hand, we know from analytical practice that at high concentrations

of KSCN, such as are employed in the colorimetric determination of iron by the thiocyanate method, the presence of aluminum salts in the solutions to be analyzed has no appreciable effect upon the accuracy of the determination.

As for the cause of the bleaching action of $Al(NO_3)_3$ at the foregoing ratios of concentrations of $Al(NO_3)_3$ and $Fe(NO_3)_3$, the following two suppositions are probable: 1) the introduction of the $Al(NO_3)_3$ changes the ionicity of the solution and hence the activity coefficient of the ions; 2) the $Al(NO_3)_3$ reacts with the KSCN, possibly forming slightly stable aluminum-thiocyanogen compounds.

A number of experiments was run to test the effect of ionicity. Instead of $Al(NO_3)_3$, $NaNO_3$ was introduced in concentrations calculated from the Lewis law. When this was done, we again observed a certain diminution in intensity of the color of the iron-thiocyanogen solution, but less so than was the case in solutions of the same ionicity but containing $Al(NO_3)_3$.

This enables us to assume that the formation of slightly stable aluminum-thiocyanogen compounds is not impossible.

Reaction of Aluminum Nitrate with Sodium Fluoride

At the beginning of this article we recalled that the reaction between aluminum and fluorine ions is rather slow, in contrast to the reactions between the ions of iron (III) and thiocyanogen or fluorine, which are quite rapid.

This is outwardly manifested in the slow intensification of the color of iron-thiocyanogen solutions containing sodium fluoride, after aluminum nitrate has been added.

Solutions of this sort are fairly complicated systems. If merely the initial substances are considered, this system may be represented as follows:

$$Al(NO_3)_3 - NAF - Fe(NO_3)_3 - KSCN - HNO_3 - H_2O.$$

This system comprises several mutually interdependent equilibria, the most important of which are:

$$Fe^{\cdot\cdot\cdot} + F' \rightleftarrows FeF^{\cdot\cdot}$$

$$Fe^{\cdot\cdot\cdot} + (SCN)' \rightleftarrows Fe(SCN)^{\cdot\cdot}$$

$$Fe(SCN)^{\cdot\cdot} + F' \rightleftarrows FeF^{\cdot\cdot} + (SCN)'$$

$$Al^{\cdot\cdot\cdot} + F' \rightleftarrows AlF^{\cdot\cdot\cdot}$$

$$Al^{\cdot\cdot\cdot} + FeF^{\cdot\cdot} \rightleftarrows AlF^{\cdot\cdot} + Fe^{\cdot\cdot\cdot}$$

$$H^{\cdot} + F' \rightleftarrows HF$$

It is obvious that the intensification of the color referred to above is the result of the formation of complex aluminum-fluorine ions, since this causes the concentration of fluorine ions to drop while increasing the concentration of the colored $Fe(SCN)^{\cdot\cdot}$.

Thus, the change in the concentration of aluminum-fluorine ions is directly related to the change in the concentration of iron-thiocyanogen ions, this relationship depending upon the ratios of the instability constants of the complex ions contributing to the equilibrium.

Therefore, the progress of a change in the concentration of the $Fe(SCN)^{\cdot\cdot}$, i.e., the intensification of the solution color, may be used to estimate the change in the concentration of the $AlF^{\cdot\cdot}$: the more intensive the color, the higher the

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The number of coordination ions depends on the fluorine or thiocyanogen concentration. At concentrations as low as those used in the solutions under analysis, chiefly the simplest coordination ions were formed.

$AlF^{\cdot\cdot}$ concentration, and hence, the farther the $Al^{\cdot\cdot\cdot} + F^{\prime} \rightarrow AlF^{\cdot\cdot}$ reaction will progress.

Evidently the achieving of a constant color intensity may serve as an indication that the reaction between the aluminum and fluorine ions has reached the state of equilibrium.

This consideration underlies our interpretation of the experimental data we secured in the investigations described below; owing to the low reaction rate, the experiment can be set up so as to make the action of the $Fe(NO_3)_3$ and KSCN comparable to the action of an indicator. We can likewise observe the decomposition of the complex aluminum-fluorine ions.

Numerous experiments established the fact that the reaction between aluminum nitrate and sodium fluoride does not reach a state of equilibrium within 7 to 8 hours. This is illustrated by Curves 1 and 2 in Fig. 2, which were plotted as follows: two solution mixtures were prepared in 0.1 N nitric acid, containing $Fe(NO_3)_3$, $Al(NO_3)_3$ and NaF. The concentration of $Al(NO_3)_3$ was 0.00163 mol/liter in Solution 1 and 0.00224 mol/liter in Solution 2. The concentration of NaF was 0.00242 mol/liter in Solution 1 and 0.00180 mol/liter in Solution 2. The $[Al(NO_3)_3]$/[NaF] ratio was 0.67 in Solution 1 and 1.25 in solution 2. The concentration of $Fe(NO_3)_3$ was 0.00020 mol/liter in these solutions, and that of KSCN was 0.00195 mol/liter.

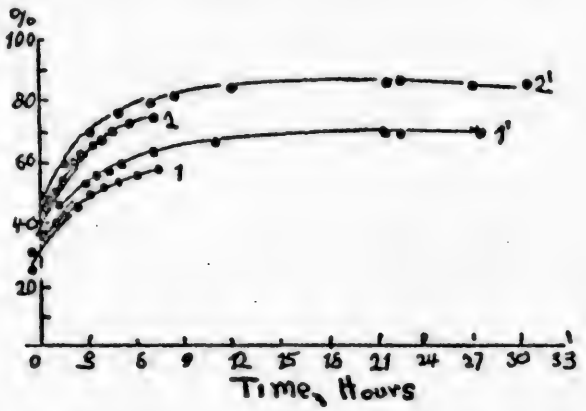

Fig. 2.

Immediately after the solutions were mixed, the optical density was measured at intervals of time for 7 to 8 hours. The time (in hours) is plotted along the axis of abscissas in Fig. 2. Time was counted from the instant the solutions were mixed. The ordinates are the relative intensity of color of the solutions under analysis, in per cent of the color intensity of an iron-thiocyanogen solution (of the same $Fe(NO_3)_3$ and KSCN concentration) containing no $Al(NO_3)_3$ or NaF (calibrating solution). The color intensity of the calibrating solution was set equal to 100.

Thus, these curves indicate the variation in the concentration of complex iron-thiocyanogen ions with the duration of the reaction between $Al(NO_3)_3$ and NaF, as well as the way in which the rise in the concentration of complex aluminum-fluorine ions varies with this time.

With this experimental setup, we were unable to investigate the solutions for longer intervals of time, owing to possible decomposition of the thiocyanate; in our subsequent experiments we therefore introduced the $Fe(NO_3)_3$ and the KSCN into previously prepared solutions of $Al(NO_3)_3$ and NaF just before measuring the optical density. We reproduce the results of two of these experiments.

Two series of solutions were prepared by mixing solutions of $Al(NO_3)_3$ and NaF in 0.1N nitric acid at fixed intervals of time (1, 2, 3, 4, 5, etc., hours). The solutions were kept in a dark place. About a day and a half after the first solution of a given series had been prepared, solutions of $Fe(NO_3)_3$ and KSCN (in 0.1 N nitric acid) were added to the test mixture, and the optical density was measured at once. Time was counted from the moment the $Al(NO_3)_3$ and NaF solutions

were mixed together until the optical density was measured. The component concentrations were the same as for Solutions 1 and 2, while the temperature was held to 15 ± 1°. The results of measurement are given by Curves 1' and 2' in Fig. 2. They show that at the given temperature the reaction between $Al(NO_3)_3$ and NaF attains a state of equilibrium after about 24 days.

The differences between the positions of Curves 1 and 1' and 2 and 2', notwithstanding the identical concentrations of their components, may be due to a considerable difference in the velocity of reaction between $Al(NO_3)_3$ and NaF, on the one hand, and $Fe(NO_3)_3$, NaF, and KSCN, on the other. This difference in the reaction rate is markedly apparent in various experimental setups.

In Experiments 1' and 2', (curves in Fig. 2), the rate at which the concentration of the colored $Fe(SCN)^{\cdot\cdot}$ rises depends on the rate of formation of the complex aluminum-fluorine ions. Curves 1 and 2 therefore characterize the progress toward equilibrium in the $Fe(NO_3)_3 - Al(NO_3)_3 - NaF - KSCN$ system.

In Experiments 1' and 2', some complex aluminum-fluorine ions had already been formed by the time the $Fe(NO_3)_3$ and the KSCN were introduced and the optical density measured. As a result, the reaction of the $Al(NO_3)_3$ with the NaF might lead to greater equilibrium, for equal intervals of time, than in Experiments 1 and 2, owing to the fact that for a large part of the time preceding the measurement of the optical density the reaction between the $Al(NO_3)_3$ and the NaF was not bound up with the presence of $Fe(NO_3)_3$ and KSCN. Moreover, the equilibrium in the $Al(NO_3)_3 - NaF$ system ought to proceed further in the direction of forming complex aluminum-fluorine ions than is the case in the $Al(NO_3)_3 - Fe(NO_3)_3 - NaF - KSCN$ system.

Owing to the great difference in the reaction rates indicated above, the $Al^{\cdot\cdot\cdot} + F' \rightleftarrows AlF^{\cdot\cdot}$ equilibrium cannot shift to the left to any appreciable extent if the $Fe(NO_3)_3$ and the KSCN are introduced into the solution just before the optical density is measured.

This is why the action of $Fe(NO_3)_3$ and KSCN in Experiments 1' and 2' (curves in Fig. 2) may be likened, to some extent, to that of an indicator, which records the situation in the $Al(NO_3)_3 - NaF$ system with respect to the equilibrium state of $Al^{\cdot\cdot\cdot} + F' \rightleftarrows AlF^{\cdot\cdot}$ at the instant the former components are added.

If measurement of the optical density is continued for some time after this, we find that the following reaction takes place: $AlF^{\cdot\cdot} + Fe^{\cdot\cdot\cdot} \rightarrow FeF^{\cdot\cdot} + Al^{\cdot\cdot\cdot}$.

Fig. 3 shows that when $Fe(NO_3)_3$ and KSCN are added to the solution of $Al(NO_3)_3$ and NaF after the $Al^{\cdot\cdot\cdot} + F' \rightleftarrows AlF^{\cdot\cdot}$ equilibrium has been attained (in this case, 30 hours after the $Al(NO_3)_3$ and NaF solutions have been mixed together,

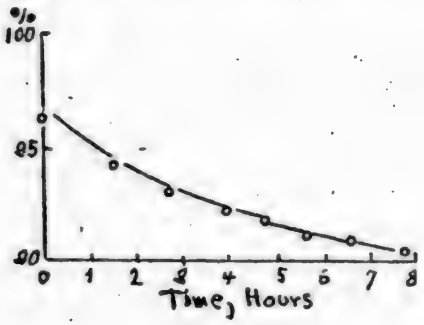

Fig. 3

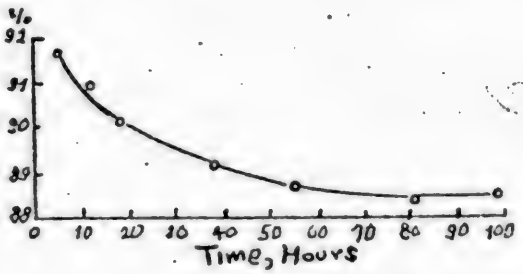

Fig. 4.

the optical density drops for a certain length of time.

Time is reckoned from the addition of the $Fe(NO_3)_3$ and the KSCN.

This is also shown in Fig. 4, which indicates that the same effect is produced by the addition of KSCN to a $Al(NO_3)_3$ – NaF – $Fe(NO_3)_3$ solution that is in equilibrium.

SUMMARY

1. It is shown that at low concentrations of KSCN the color of an iron-thiocyanogen solution is weakened by aluminum nitrate.

It is assumed that this involves the formation of slightly stable aluminum-thiocyanogen compdunds.

2. It is shown that the reaction rate of the formation of complex aluminum fluorine ions is low when $Al(NO_3)_3$ and NaF react together in an aqueous solution of nitric acid.

Equilibrium is reached within about one day at 15°.

3. When determining fluorine colorimetrically by the iron-thiocyanogen method, aluminum must be first eliminated from the solution.

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Received July 1, 1948.

THE EFFECT OF SOLVENTS UPON THE DISSOCIATION OF A COBALT-THIOCYANOGEN COORDINATION COMPOUND

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Among the numerous research papers on the thiocyanogen and chlorine coordination compounds of cobalt, there are many papers on the properties of these compounds in nonaqueous solutions. The objective of these papers, however, was a study of the absorption spectra of solutions of particular compounds ($CoCl_2$, $K_2Co(CNS)_4$ etc.). The literature on the halogen and thiocyanogen coordination compounds of cobalt does not discuss the problem of the stability of these coordination compounds in different solvents. In general, extremely little attention has been paid to this question in connection with other coordination compounds as well. And yet it is of considerable interest for the general chemistry of coordination compounds, as we know that the properties of these compounds are most strikingly manifested in solution. This question is also of importance for the practical application of coordination compounds in chemical analysis, since the introduction of nonaqueous solvents (alcohol, acetone, etc.) is the customary procedure used to lessen the dissociation of coordination compounds and to effect their more complete formation in solution. But no research has yet been done on this important procedure; we possess no general conclusions at all nor any quantitative data.

The problem of the effect of solvents upon the dissociation of electrolytes has been the subject of considerable and thoroughgoing research with regard to salts of the strong-electrolyte type and to various acids (including weak ones). Some of the general conclusions of these research papers have been used in the present article, since the cobalt thiocyanates are weak complex electrolytes. It was the objective of the present paper to study the dissociation of a cobalt-thiocyanogen coordination compound in mixtures of various solvents with water. The solvent studied in greatest detail was acetone, since the latter is most often employed in the colorimetric determination of cobalt. Other solvents investigated included dioxane, which has an extremely low dielectric constant (2.28), and ethanol. We also did research on acetic acid as a solvent; it has a low dielectric constant (7.1) but is an acid solvent that greatly lowers the dissociation constant of acids, including thiocyanic acid. Formic acid (dielectric constant = 47.4) was also investigated as a standard of comparison for acetic acid.

Solutions of Cobalt-Thiocyanogen Coordination Compounds in Mixtures of Acetone and Water

The formation of a coordination compound in the reaction of a central cation B with a coordinated anion A may be diagrammatically represented as an equilibrium:

$$B + A \rightleftarrows BA \qquad (1)$$

The dissociation constant of the coordination compound is:

$$K_{compl.} = \frac{[B][A]}{[BA]} . \qquad (2)$$

The reciprocal of the constant may serve as a measure of the coordination compound's stability, since the free energy of the reaction between B and A is $F_{compl.} = -RT \ln K_{compl.}$. It is obvious from Equations (1) and (2) that at low concentrations of the coordination ion A, only little of the coordination compound will be formed, when $[A] \ll K_{compl.}$. As the concentration of A is increased to a value that numerically approaches that of $K_{compl.}$, the equilibrium (1) will be shifted to the right, and at large excesses of A, viz, when $[A] \gg K_{compl.}$, the formation of a coordination compound will be practically complete. It is obvious from Equation (2) that at a certain value of $A = K_{compl.}$, we get $[B] = [BA] = \frac{1}{2}[B_{total}]$. When the coordination compound BA is colored, and the central ion B is colorless (in a given portion of the spectrum), such a solution will evidently possess half the maximum possible color (for the given total concentration of B). Thus, the problem boils down to the experimental determination of the concentration of the excess A required to produce an optical density $D_{\frac{1}{2}}$ equal to half of D_{max}. The latter quantity is likewise determined experimentally as the optical density produced with a large excess of A, D_{max} not undergoing any further change as the concentration of A is increased still further, since all the B present is already combined into the coordination compound BA.

This simple scheme is the foundation of our further discussion, although the equilibria in the $Co^{++}_{dissolved} - CNS^{-}_{dissolved}$ system are more complicated.

As has been shown previously [1], with small quantities of CNS^-, at most one weakly colored complex ion $CoCNS^+$ is formed, followed by other groups in succession, with the absorption of the solution at the red end of the spectrum increasing.

The most intensely colored is the complex anion $Co(CNS)_4$. Consideration of all the step-by-step equilibria for various solvents would require too much space. As has been shown previously [2,3,4], the separate step-by-step dissociation constants are usually related in some definite manner, dependent upon the coordination number, but not on the nature of the components; if one of the step-by-step constants, depending on the individual nature of the components, is known, the other step-by-step constants can be computed. In the present research project we were interested in the change in the binding energy of the components of the complex ion (Co^{++} and CNS^-) as a function of the solvent; it was therefore immaterial, generally speaking, what step-by-step constant was used as a basis for the comparison of the effects of various solvents. The attainment of $D_{1/2}$ was easiest and most dependable to determine experimentally. In accordance with what has been set forth above, the thiocyanogen concentration required to attain $D_{1/2}$ can serve as a measure of $K_{compl.}$* as well as a measure of the change of this constant with a change in the composition of the solvent. The experiments were set up for the following acetone – water ratios: 1) anhydrous acetone; 2) 90% acetone and 10% water by volume; 3) 75% acetone and 25% water; 4) 50% acetone and 50% water; and 5) 25% acetone and 75% water.

Our initial solutions were: a 0.52 molar solution of cobalt nitrate in acetone, and a 0.52 molar solution of potassium or ammonium thiocyanate in acetone. Potassium thiocyanate is more stable in acetone solutions, but in solutions containing a little water its reaction with cobalt nitrate causes the precipitation of KNO_3 which is insoluble in anhydrous acetone and dissolves at the given concentrations only when approximately 10% of water is present.

The titers of the solutions were established by the usual methods: gravi-

*More precisely, not the total concentration, but $[CNS_{total}] - 2[Co^{++}_{comb}]$ if we assume that the undissociated molecule $Co(CNS)_2$ is formed at the optical density $D_{\frac{1}{2}}(\frac{1}{2} D_{max})$.

**It can be shown that this value $[CNS] = \sqrt{K_2 K_3}$ where K_2 and K_3 are the step by step constants $Co(CNS)_2$ and $Co(CNS)_3$.

metrically (for the cobalt), and volumetrically (for the thiocyanates). The total concentration of cobalt was $5 \cdot 10^{-3}$ mol after the colored solutions had been prepared. The color intensity was measured with a Pulfrich photometer, provided with light filters that passed 610 and 680 mμ. The results of measurements for 610 mμ are given below.

The results are shown in Fig. 1. The values of log [CNS⁻] are plotted as abscissas. The ordinates are the percentage of cobalt combined into the blue-colored complex ion, i.e., the optical-density ratio (log I_0/I) under the given conditions in per cent of the maximum optical density produced with large excesses of the thiocyanate. This method of expressing the results is most convenient, since it eliminates the influence of certain shifts in the absorption spectra when the composition of the solvent is changed.

The first curve shows the results of measurement in anhydrous acetone; the percentage of water in the solution is given alongside the other curves. As may be seen from Fig. 1, the curves showing the binding of cobalt in a colored thiocyanogen complex ion are fairly symmetrical, which speaks in favor of the identical overall nature of the equilibria for various water-acetone ratios. But as the percentage of water rises, more and more thiocyanogen is required to bind the cobalt in the complex ion.

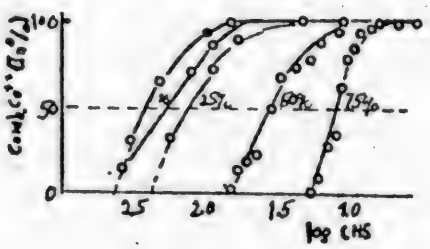

Fig. 1.

It was also thought of interest to find the relationship between $K_{compl.}$ and the volumetric ratio of water to acetone, and thence its variation with the dielectric constant of their mixture.

According to Silberstein [5], the dielectric constant of a mixture may be approximately calculated from its volumetric ratio by means of the equation:

$$DC = \frac{V}{100} DC_1 + \frac{100 - V}{100} DC_2, \qquad (3)$$

where V and DC_1 are the volumetric percentage and the dielectric constant of one liquid, and $(100 - V)$ and DC_2 are those of the other. For various mixtures of the solvent with water we did not know the value of the dielectric constant; in order to use a method of computation that was generally applicable to all cases, we therefore employed the approximation formula (3). The results of our computations of the variation of K_{compl} with DC are given in Table 1.

TABLE 1

Percent of water by volume in the acetone mixture	Concentration of [CNS^-_{total}] in mols at $D_{1/2}$	Concentration in mols of [CSN^-_{free}] = [CNS^-_{total}] + + 2[Co^{++}] at $D_{1/2}$	$pK_{compl} = -\log K_{compl}$	DC from Equation (3)	$\frac{1}{DC}$
1	2	3	4	5	6
10	$6 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	2.4	27	0.037
25	$1.2 \cdot 10^{-2}$	10^{-2}	2.0	38	0.026
50	$2.7 \cdot 10^{-2}$	$2.5 \cdot 10^{-2}$	1.6	51	0.020
75	$7.2 \cdot 10^{-2}$	$7.0 \cdot 10^{-2}$	1.15	66	0.015
100	3.0	3.0	-0.5	81	0.012

The first column of the table gives the per cent of water by volume in the mixture. Column 2 gives the values of the total concentration of thiocyanogen at which half the maximum color was attained. These values were taken from the experimental data used in plotting the curves of Fig. 1, as well as by interpolation in the data of Fig. 1. As has been indicated above, the concentration of the potassium (or ammonium) thiocyanate at which 50% of the maximum coloring is attained equals $[CNS^-] = K_{compl.}$. Moreover, separate experiments were set up as follows to determine this value. Some Co^{++} (0.5 ml of a 0.01 molar solution) was directly mixed in the photometer cell with a large excess of NH_4CNS (2 to 3 ml of a 1.0 molar solution), and the optical density was measured. In the second experiment, the concentration of Co^{++} was doubled over that of the first experiment, and then enough thiocyanate was added to produce $Co(CNS)_2$. If it was found that the optical density was less than in the previous experiment, more thiocyanate was added from a microburette until the color was the same as in the first test. Since the overall cobalt concentration in the second test was twice that in the first, when the optical density was the same for both solutions, half as much cobalt was combined in the second solution. This method eliminates any error of the optical instrument. The $[CNS^-_{free}]$ is calculated from the amount of cyanate consumed. Column 3 gives the concentration of free thiocyanogen.* Column 4 shows the value of $pK_{compl.} = [CNS^-_{free}]$ at $D_{1/2}$. Column 5 gives the value of DC, computed from Equation (3), while the value of 1/DC is given in Column 6.

The procedure outlined above gives results that are in good agreement with those of Fig. 1 for mixtures of water and acetone; in our work with other solvents we therefore set up only experiments using this method. These data are listed in Table 2 below.** According to Kablukov [6], Nernst [7], and Thomson, the dissociation of electrolytes depends upon the dielectric constant of the solvent. As we know, Brönsted [8] has shown that in electrolytic dissociation a straight-line relationship should exist beween the logarithm of the dissociation constant and the magnitude of the dielectric constant of the solvent.

In our experiments with each individual solvent, especially in the region from 10% to 75% water, we find that the results are not far from a straight-line relationship between $-\log K_{compl.}$ and 1/DC. But, when we examine all the results together, it is quite clear that such a relationship does not exist over a wide range of experimental conditions. In all instances the value of $pK_{compl.}$ deviates sharply from a straight line in pure water; the addition of relatively small quantities of the nonaqueous solvent results in a marked rise in the stability of the complex ion, i.e., a drop in $K_{compl.}$ Thus, to bind half the cobalt in the blue thiocyanogen complex ion of the aqueous solution, thiocyanate has to be added until the thiocyanogen concentration is some 3.0 gram-ions per liter. The adding of 25% acetone, ethanol, or other solvents lowers the necessary thiocyanate concentration 100 times and more. Further addition of a nonaqueous solvent aids in formation of the complex ion, but much less effectively. At a low water concentration the course of $-\log K_{compl.}$ as a function of 1/DC for each solvent exhibits a slight and fairly constant deviation from the vertical; shifting to 100% water produces a quite sharp change, entailing a marked deviation from a straight-line relationship. The variation of $-\log K_{compl.}$ as a function of 1/DC is upset even more markedly when the data for the various solvents are compared. Dioxane has the smallest DC though the complex ion is dissociated least in acetone, rather than in dioxane. In anhydrous acetone, for instance, practically all the thiocyanogen is combined with the cobalt, but when the acetone contains 10% of water, $4 \cdot 10^{-3}$ gram ion of thiocyanogen per liter suffices to combine half of the cobalt into the blue thiocyanate complex ion. A mixture of dioxane with 25% of water has nearly the same DC as anhydrous acetone, but an excess of $1.5 \cdot 10^{-3}$ gram-ion of thiocyanogen per liter suffices to bind half the cobalt The DC of formic acid is higher than that of dioxane and twice as high as that of acetone, yet when

*See footnote p. 238 this text.

**The initial cobalt concentration was constant in all the experiments of Tables 1 and 2: 0.002 gram-ions per liter.

TABLE 2

Solvent	Percent of water by vol. in the solvent	Concentration of $[CNS^-_{total}]$ in mols at $D_{1/2}$ max.	Concentration in mols of $[CNS^-_{free}] = [CNS^-_{total}] - 2[Co^{++}]$ at $D_{1/2}$	$pK_{compl.}$	DC from Equation 3	1 DC
1	2	3	4	5	6	7
Acetic acid	10	10^{-2}	$0.9 \cdot 10^{-2}$	2.1	14	0.071
	25	$2.1 \cdot 10^{-2}$	$1.9 \cdot 10^{-2}$	1.7	36	0.043
	50	$3.8 \cdot 10^{-2}$	$3.6 \cdot 10^{-2}$	1.4	44	0.023
	75	$4.7 \cdot 10^{-2}$	$4.5 \cdot 10^{-2}$	1.3	63	0.016
Dioxane	10	$0.9 \cdot 10^{-2}$	$0.7 \cdot 10^{-2}$	2.2	10	0.100
	25	$1.7 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	1.8	22	0.045
	50	$3 \cdot 10^{-2}$	$2.8 \cdot 10^{-2}$	1.6	42	0.024
	75	$4.4 \cdot 10^{-2}$	$4.2 \cdot 10^{-2}$	1.4	62	0.016
Ethanol	10	10^{-2}	$0.8 \cdot 10^{-2}$	2.1	32	0.031
	25	$2.1 \cdot 10^{-2}$	$1.9 \cdot 10^{-2}$	1.7	40	0.025
	50	$3.6 \cdot 10^{-2}$	$3.4 \cdot 10^{-2}$	1.5	54	0.019
	75	$8.6 \cdot 10^{-2}$	$8.4 \cdot 10^{-2}$	1.1	67	0.015
Formic acid	10	$2.3 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$	1.7	51	0.020
	25	$4 \cdot 10^{-2}$	$3.8 \cdot 10^{-2}$	1.4	52	0.019
	50	$10 \cdot 10^{-2}$	$9.8 \cdot 10^{-2}$	1.0	64	0.016
	75	$15 \cdot 10^{-2}$	$15 \cdot 10^{-2}$	0.9	73	0.014
Water	100	3.0	3.0	-0.5	81	0.012

these solvents contain 10% of water, only a relatively small excess of CNS^- is needed to achieve the same degree of binding the cobalt in a complex ion. In formic acid only three times as many CNS^- ions are required as in dioxane. Furthermore, if we bear in mind that formic acid converts part of the CNS^- ions into HCNS molecules, the difference between the dissociation of the cobalt-thiocyanogen complex ion in dioxane and in formic acid becomes even less.

For comparison, we reproduce Fig. 2, in which the abscissas are $-\log K_{compl.}$, and the ordinates are 1/DC. The individual points for the various solvents are plotted in the graph. The curves clearly exhibit the deviation of the function from linearity, as well as the markedly individual nature of the curves for each solvent; hence, the properties of these solvents cannot be expressed by their dielectric constants.

Comparison of the variation of the dissociation constant of the cobalt-thiocyanogen complex ion with the volumetric proportions of the various solvents with water yields a much more general law. The abscissas in Fig. 3 are the percentages of water in mixtures with various solvents, the ordinates being $-\log K_{compl.}$

The results we have obtained may thus be described by much simpler characteristics. Ignoring the details of the reaction mechanism, we may assume that certain nonaqueous solvents bind water when added to an aqueous solution of a cobalt-thiocyanogen complex ion, thus facilitating the elimination of water from the inner sphere of the aquo-cobalt complex ion. Thus, the equilibrium in the

equation: $[Co \cdot 4H_2O]^{++} + 4CNS^- \rightleftarrows [Co(CNS)_4]^{--} + 4H_2O$ is shifted to the right, owing to the binding of water by the nonaqueous solvent. In this latter respect, the different solvents, which are mixed with water in any proportions, act approximately alike, no matter what their DC.

The somewhat singular behavior of formic acid may be explained as due to its acid properties, which lower the dissociation of the thiocyanic acid, thus

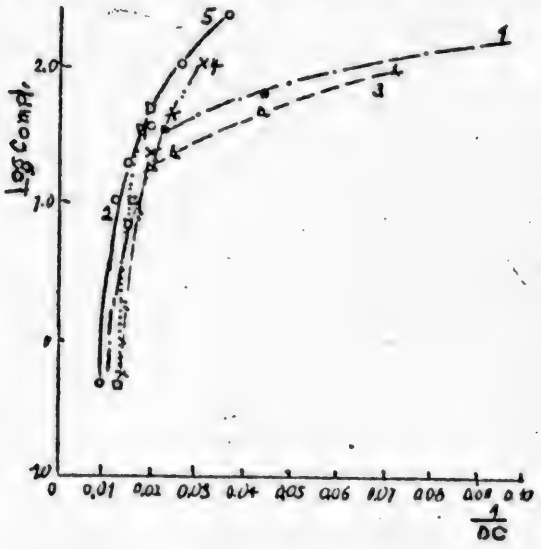

Fig. 2.
1-Dioxane; 2-formic acid; 3-acetic acid; 4-ethanol; 5-acetone.

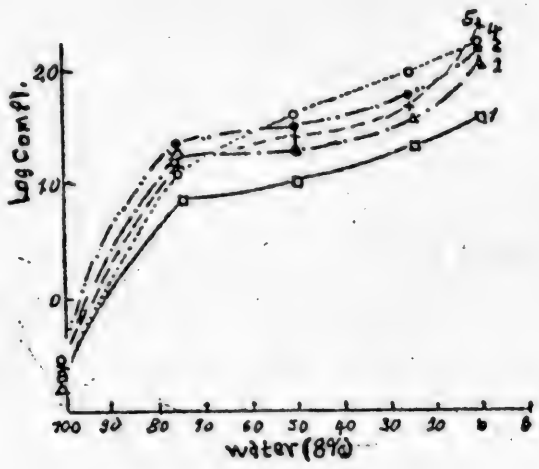

Fig. 3
1-Formic acid; 2-acetic acid; 3-dioxane; 4-acetone; 5-ethanol.

binding the CNS^- ion into a HCNS molecule and hampering the formation of the complex ion. Solutions of the complex ion in formic acid are also characterized by singular behavior toward other factors as well, such as the action of pyridine. Pyridine forms a stable complex ion with Co^{++} ions, readily displacing the thiocyanogen ion from the inner sphere and causing a color change from blue to red in various solvents. But if pyridine is added to a solution of the cobalt-thiocyanogen complex ion in HCOOH containing an insufficient excess of thiocyanogen, what happens is as follows. The first batch of pyridine causes a blue color to appear, apparently owing to a diminution of the acidity and, as a result, an increase in the concentration of thiocyanogen ions. Further additions of pyridine cause the blue color to turn red again. Notwithstanding the singularities in the behavior of formic acid, the curves of Fig. 3 indicate that, on the whole, the various non-aqueous solvents investigated by us have approximately the same effect upon the stability of the Co – CNS complex ion, no matter what their DC may be. The lowest dissociation is found in acetone.

SUMMARY

The formation of the blue thiocyanogen complex ion of cobalt in various solvents has been investigated, and the value of the dissociation constant of the complex ion has been calculated for these various conditions.

Acetone, dioxane, ethanol, formic acid, and acetic acid were used as solvents, as well as their mixtures with 10, 25, 50, and 75% of water. These non-aqueous solvents greatly diminish the dissociation of the complex ion, acetone

exhibiting the lowest constant.

It has been shown that there is no straight-line relationship between the pK of the complex ion and the reciprocal of the dielectric constant of the solvent mixture. At identical water-nonaqueous solvent volumetric ratios, all the solvents mentioned cause approximately the same change in the dissociation constant of the complex ion.

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Received July 2, 1948

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*See CB translation p. a261 ff.

THE EFFECT OF THE FORMATION OF A COORDINATION COMPOUND UPON INTERCHANGE IN RECIPROCAL TERNARY SYSTEMS

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The course of a double decomposition reaction in reciprocal systems:

$$AX + BY \rightleftarrows AY + BX \qquad (I)$$

may be largely determined a priori from the nominal thermochemical effect of the exchange reaction, as computed from the heats of formation of its components; heats of formation are usually given as at 25°. Depending on the magnitude of the thermal effect, we obtain reversible, irreversible, or singular reciprocal systems of the diagonal type, which may be divided into phase simplexes – triangles [1] (Fig. 1).

In diagonal systems there are two conjugate sections, both of them diagonals. The total heat of formation of the components of one of the diagonals will always be greater than that of the other; hence, the diagonal with superior energy will be stable and will triangulate the composition square.

If a clearly outstanding compound is formed in one of the lateral binary systems, triangulation of the square of the reciprocal system need not start at the corners, but at the point denoting the composition of the binary side compound. When this is so, the triangulating secant connects the point of the compound's composition with the opposite components of the composition square. We may call such secants adiagonal, and call the reciprocal systems that can be divided into simplexes of this type adiagonal systems [2,3] (Fig. 2).

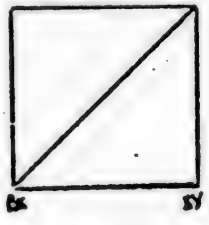

Fig. 1

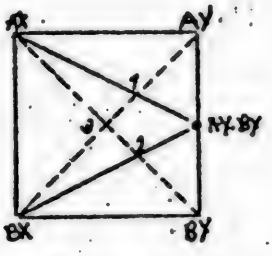

Fig. 2

In adiagonal systems, a binary compound will be formed from the components of the diagonals at the point where the diagonals intersect the adiagonal secants (Points 1 and 2, Fig. 2.).

$$2AY + BX \longrightarrow AY \cdot BY + AX \qquad (II)$$

$$2BY + AX \longrightarrow AY \cdot BY + BX \qquad (III)$$

If we take the sum of the heats of formation of the compound and of one of the components lying opposite [the right-hand sides of Equations (II) and (III), components of the adiagonal section], in the adiagonal type it will be higher than the sum of the heats of formation of the diagonal components [left-hand sides of Equations (II)

and (III)], i.e., the reaction involving the formation of a coordination compound will predominate in the system.

We define the term "formation of a coordination compound" to mean the formation of a salt of the double-salt type. The heat of formation of a complex salt from the elements consists of three components: the heats of formation of the two initial salts and the heat of formation of the complex salt from the two component salts.

In Fig. 2 we have four possible secants, constituting three conjugate pairs; they intersect at the points 1, 2, and 3. In the adiagonal type the only triangulating secants will be those starting at the apex of the compound, i.e., the reactions corresponding to Points 1 and 2 will take place [the equations (II) and (III) described above]. There is another possible arrangement of the triangulating secants with the coordination compound in one of the lateral binary systems, i.e., one starts at the apex of the coordination compound, while the other lies along the diagonal (Fig. 3). When this is the case, the sum of the heats of formation of the components of one of the diagonals is greater than the sum of the heats of formation of the components of the conjugate adiagonal section (Point 1).

On the other section, starting at the apex of the coordination compound, the sum of the heats of formation of the components of the adiagonal section is greater than the heats of formation of the components of the diagonal section, i.e., the adiagonal pair (Point 2) will be more stable from the energy standpoint. In this latter case, the reactions taking place within the system are represented by the following equations:

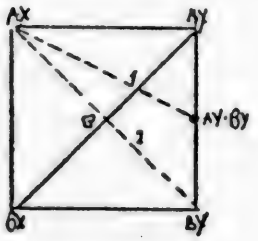

Fig. 3.

$$AY \cdot BY + AX \rightarrow BX + BY \qquad (IV)$$

$$2BY + AX \rightarrow AY \cdot BY + BX \qquad (V)$$

The triangulating, i.e., the stable, sections are the diagonal BX–AY and the adiagonal section BX–AY·BY.

In the cases discussed above we did not differentiate between the stable secants; in cases 2 and 3, one of the two stable secants is doubtless superior to the other from the energy standpoint, and this ought to be reflected in the geometrical form of the system's crystallization surface. A more sharply contoured pair of ridges of the components of the prevailing stable system will correspond to a more stable section, and the transition point (the Van Rijn-Van Alkemade point) should occur at a higher temperature than the corresponding point for a subordinate section. As we know from the theory of ternary systems, with a congruent compound on one side the triangulating section will be like a binary system, while with an incongruent system, somewhere along this section one of the components of the melts of this section may first separate out, giving rise to this compound (usually more refractory). During the ensuing process, however, the crystals of the initially separated component, reacting with the melt, are fully converted at the nonvariant ternary transition point into a coordination compound if the process is in equilibrium; this latter compound vanishes completely as an independent phase.

After equilibrium crystallization is complete, the solidified alloys of this section will contain only two phases, as with a stable section, starting at the point of the congruent compound. Applying this relationship to interdependent systems, we get two basic variants for the case illustrated in Fig. 3, which are reproduced in Figs. 4 and 5. In Fig. 4 the diagonal section predominates, the adiagonal one being subordinate; this adiagonal section may or may not possess the characteristics of a binary system, but in either case it must be a triangulating section. In

Fig. 5 the adiagonal section predominates, and the diagonal section is the subordinate one.

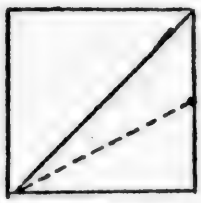

Fig. 4.

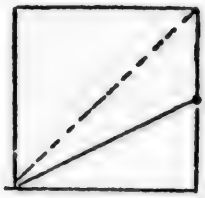

Fig. 5

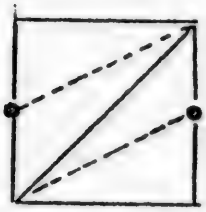

Fig. 6.

In our next paper this type is illustrated by a diagram of the reciprocal system Ca,Ba‖ F, Cl [12], in which the subordinate diagonal section $CaF_2 - CaCl_2$ possesses the characteristics of a binary system.

Since the type of reciprocal system illustrated in Fig. 5 is a new one, we propose to call it "adiagonal with a subordinate diagonal section".

When there are two compounds at opposite sides, a distinction must again be made between two fundamental cases:

1) The double decomposition reaction predominates (Fig. 6); The principal triangulation occurs along the diagonal, with further triangulation of the two resulting triangles taking place in the same direction as in Fig. 6.

2) The reaction involving the formation of a coordination compound predominates, with the two components failing to form double-decomposition products when they react together; when this is so, the square of the reciprocal system is first divided into two rectangles (tetragons in the general case), which in turn may be looked upon as new reciprocal systems and subjected to further triangulation, as in Figs. 7 and 8.

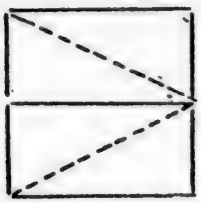

Fig. 7.

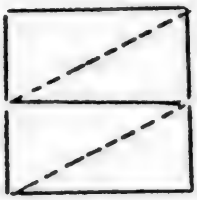

Fig. 8.

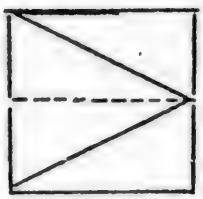

Fig. 9.

3) One of the compounds is markedly predominant, resulting in an initial adiagonal cleavage with ensuing triangulation of the basic internal triangle, along the dotted line in Fig. 9.

4) In addition to the formation of coordination compounds, continuous series of solid solutions of any two pairs of components are formed, as well as continuous series of solid solutions of the coordination compounds (Fig. 10); the fundamental prerequisite for this type is the absence of any sharply defined shift in the exchange reaction, as otherwise we would get triangulation as in Fig. 6.

5) The system has one sharply defined adiagonal section, while the other triangulating sections may be represented as secants that do not possess the characteristics of binary systems (Fig. 11). Reciprocal systems in which a section connecting two coordination compounds on two opposite sides is a triangulating section

(Figs. 7, 8, 9, and 10) may be placed in a special class; we call this the "zonal type of reciprocal systems." What is characteristic of this type is the circum-

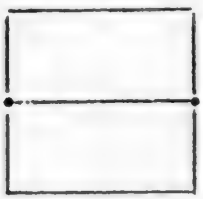

Fig. 10.

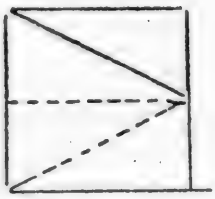

Fig. 11

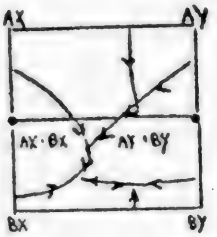

Fig. 12.

stance that no pair of diagonal components is in contact with its crystallization regions, for they are separated by the abutting crystallization regions of the two coordination compounds.

Figs. 12 and 13 illustrate two elementary examples. When the transverse section is like a binary system with a transition point (Van Rijn – Van Alkemade point), we get the relationship shown in Fig. 12; if not, we get a somewhat differen configuration, as shown in Fig. 13. The zonal type is likewise of interest because it first divides the reciprocal-system square into two tetragons, which – as coordination figures – undergo subsequent triangulation, with reciprocal displacement [Equation (VII)] rather than double decomposition taking place in each tetragon. A similar reciprocal displacement reaction [Equation (VI)] occurs in the simplest types of ternary systems, Fig. 14, with two compounds formed on each side:

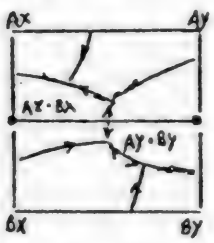

Fig. 13

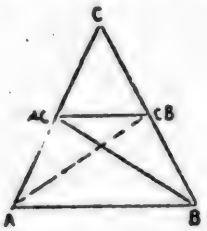

Fig. 14

$$CB + A \rightarrow AC + B \quad \text{(VI)}$$

$$AX \cdot BX + AY \rightarrow AX + AY \cdot BX \quad \text{(VII)}.$$

The difference between the chemical action in the systems represented in Figs. 7-10 and that in the systems of Figs. 6 and 11 should be emphasized.

In the zonal systems (Figs. 7-10), the two complex salts do not interact with each other; they either form a eutectic mixture (Figs. 7-9) or solid solutions (Fig. 10).

In systems of the diagonal type (Fig. 6), the reaction between the two complex salts results in their decomposition, yielding the initial components:

$$AX \cdot BX + AY \cdot BY \rightarrow 2AX + 2B.$$

SUMMARY

In this paper we have briefly considered only two cases: 1) when a single coordination compound is formed, and 2) when two coordination compounds are formed at opposite sides of reciprocal systems. The treatment proposed in this paper for reciprocal systems in which coordination compounds are formed has been worked out in detail by us for all other cases, involving the formation of two compounds along one side or on two adjacent sides, as well as for all cases in which there are many compounds on the sides of the square of the reciprocal system as well as within the composition square of ternary reciprocal systems; we have applied these conditions to quaternary and even higher reciprocal systems.

The fundamental types of reciprocal systems, as derived by us from energy and

general topological considerations, may be illustrated by the reciprocal systems we have investigated. We list below some of the most typical systems:

Ag, Hg||Cl, I (Fig. 1) [4]
Li, Sr||F, Cl (Fig. 2) [5]
Na, Sr||F, Cl (Fig. 3) [6]
K, Na||F, B_4O_7 (Fig. 4) [7]
Li, K ||Cl, SO_4 (Fig. 5) [8]
Ag, Te||Cl, SO_4 (Fig. 6) [9]
Li, K ||SO_4, WO_4 (Fig. 8, 12) [10]
Sr, Ba||F, Cl (Fig. 10) [11]
Ca, Ba||F, Cl (Fig. 11) [12]
K, Cd||Cl, SO_4 (Fig. 12) [13]

We shall not describe these systems for reasons of space.

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Received July 21, 1948.

*Obvious typo.

THE ISOMERIZATION OF AMMONIUM THIOCYANATE IN SOLUTIONS

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It is known that ammonium thiocyanate isomerizes to thiourea in the molten state. At temperatures of 150-180° this reaction is rather rapid, attaining equilibrium within 45-50 minutes with the formation of 25% of thiourea.

Kappana [1] conducted extensive research upon the kinetics of the isomerization of ammonium thiocyanate to thiourea in the fused state at temperatures ranging from 140 to 180°. This reaction has also been applied in practice recently; Nosalevich, Kukushkin, and Simonenko [2] have established the optimum conditions for the process, based upon an industrial method for the production of thiourea from the ammonium thiocyanate obtained in coke chemistry.

Urazovsky and Sidorov [3] demonstrated the feasibility of isomerizing ammonium thiocyanate in the solid state; this is of considerable theoretical interest in view of current notions of the mobility of the component parts of a molecule in a crystal lattice during Type-2 phase transformations. As for the isomerization of ammonium thiocyanate in solutions, there are no thorough investigations that give the kinetic measurements of this reaction. The available statement concerning equilibrium between thiourea and ammonium thiocyanate in propyl and butyl alcohol [4] does not deal with either the problems of the kinetics or the mechanism of this conversion.

The absence of research on the conversion of ammonium thiocyanate into thiourea in solutions is apparently due to the difficulty of finding a suitable solvent, as ammonium thiocyanate is only slightly soluble in organic solvents, while there is no point in attempting isomerization in water, owing to electrolytic dissociation. In the present research project we aimed at finding the conditions – solvent and temperature – at which ammonium thiocyanate would isomerize at a satisfactory rate. Moreover, expecting to effect the conversion in solution, we proposed to ascertain whether the reaction took place at lower temperatures than in the fused state, i.e., whether the solvent ensures the isomerization of the separate molecules, or a certain temperature range must first be attained before the parts of the molecule rotate into the crystalline phase. On the other hand, we were interested in the feasibility of more complete conversion, i.e., a shift in the equilibrium under the influence of the solvent toward the formation of thiourea, which would have practical value.

With this in mind we tried out a number of solvents, selecting them with regard to their dissolving ammonium thiocyanate and their having as high a boiling point as possible, in order to enable us to carry out the reaction in the 120-150° range. The latter factor proved to be absolutely indispensable, as the reaction failed to proceed in any of the solvents tested at the lower limit of the foregoing temperature range.

Phenol proved to be the most effective medium in which to carry out the isomerization of ammonium thiocyanate in solution. Though the solubility of ammonium thiocyanate in phenol is extremely low, hardly amounting to 0.1% at temperatures in excess of 100°, nonetheless carrying out the reaction in this medium guaranteed a rather efficient process.

The experiments were run at 120, 130, and 140°. A flask with known amounts of phenol and ammonium thiocyanate was plunged into a thermostat bath, which could be regulated to within 0.5°. Enough ammonium thiocyanate was taken to form a saturated solution with a slight excess of the bottom phase at the test temperature. As the reaction proceeded (after 40 to 60 minutes), the saturation of the solution disappeared (this was judged by a discontinuity in the curve of ammonium-thiocyanate concentration; cf Table 1); time was counted as from this instant for our kinetic calculations. A sample of 5 ml of the solution was taken from the flask at fixed intervals of time and analyzed for residual ammonium thiocyanate by the customary argentometric method. Table 1, which gives the experimental data for isomerization at 130°, furnishes an idea of the course of the process. It also gives the constants of action, calculated from the equation for a first-order reaction.

TABLE 1

Sample No.	Time, minutes	Ml of $AgNO_3$ used in titrating the sample	Concentration of NH_4CNS, $(a-x)\cdot 10^2$, in mols/liter	Constant of action, $k \cdot 10^2$	Degree of conversion, per cent	Remarks
1	20	8.8				Initial concentration of ammonium thiocyanate was 0.0731 g per 100 ml phenol, i.e., $0.77\cdot 10^2$ mol/liter
2	30	9.0				
3	50	11.3				
4	60	12.6				
		Saturation disappeared				
5	0	12.6	0.630	–	0	
6	15	11.0	0.550	0.900	12.7	
7	25	10.1	0.505	0.882	19.9	
8	35	9.1	0.455	0.930	27.8	
9	45	8.4	0.420	0.900	33.4	
10	52	7.7	0.385	0.945	39.1	
11	60	7.3	0.365	0.901	42.1	
12	77	6.2	0.310	0.953	50.9	60% of the initial quantity.
13	87	6.2	–	–		
			Average	0.916		

As we see in Table 1 (Col 3), the quantity of ammonium thiocyanate increases with time during the first stage of the experiment, notwithstanding its conversion into thiourea. This indicates the slowness of dissolving process, which takes about an hour and overlaps the consumption of the isomerized thiocyanate as long as the bottom phase is present. In the second phase of the experiment, after saturation no longer exists, the quantity of the thiocyanate decreases regularly in accordance with the equation for a first order-reaction.

The singular catalytic action of the thiourea formed upon the solubility rate of the ammonium thiocyanate, which we noticed after adding a few cubic centimeters of reacted solution to it, is worthy of note: the crystals dissolved quickly. A batch of the thiocyanate, even smaller than corresponds to its solubility, dissolves slowly in fresh phenol, however. Thus, the presence of thiourea, which facilitates solution, accelerates the process as a whole, while, by accelerating the solubility of the ammonium thiocyanate, it also facilitates the latter's isomerization in large quantities. This circumstance increases the practical value of phenol as a solvent for this reaction; as for the reason for this seemingly paradoxical behavior of a reaction product, it is apparently due to the well-known peculiarities in the behavior of thiourea with phenol.

Table 2 is a summary of data on the velocity constants of isomerization at three temperatures, as well as the degree of conversion and the computed activation energy. It also gives the corresponding figures for a melt at 140° [1], for the sake of comparison.

Table 2

Temperature, °	Constant of action, $k \cdot 10^2$	Degree of conversion, per cent	Activation energy, cal. mol.	Remarks
120	0.440	48		
130	0.916	80	22725	
140	1.807	65		
140	0.099	28	32390	Fused (after Kappanna)

Examination of the data given in Table 2 quite clearly shows the essential difference in the progress of the isomerization of ammonium thiocyanate in the fused state and in phenol. In the phenol solution, the reaction sets in at a lower temperature than in the melt. The reaction rate in the phenol is nearly 20 times that in the melt. The degree of conversion is more than double. The energy of activation is nearly 10,000 calories lower.

Thus, the use of phenol as a reaction medium greatly promotes the isomerization of ammonium thiocyanate to thiourea, apparently facilitating the formation of an active complex group with the phenol molecule. Moreover, the part played by the phenol is not confined merely to its catalytic action, since it also results in a shift of the equilibrium toward a more farreaching conversion of the thiocyanate. The latter circumstance is evidently due to the great affinity of the reaction product, thiourea, for the solvent.

SUMMARY

1. The kinetics of the isomerization of ammonium thiocyanate to thiourea in phenol has been investigated at 120, 130, and 140°.

2. It has been established that phenol as a solvent greatly facilitates the process of isomerization, compared to the melt, increasing the reaction rate (nearly 20 times) and shifting the equilibrium to a 65% conversion into thiourea at 140°. The temperature of the onset of isomerization is also lowered to 120°.

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Received July 23, 1948

RESEARCH ON THE ENOLIZATION OF CARBONYL COMPOUNDS BY THE CHRONOMETRIC-TURBIDITY METHOD

III. THE TURBIDITY RATE OF ALKALINE MIXTURES OF ACETONE AND IODINE IN THE PRESENCE OF FREE IODINE

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Our investigations of the reaction of iodine with acetone in an alkaline medium, by means of the turbidity chronometric method [1,2] revealed interesting singularities of this reaction. We showed that in reagent mixtures that do not contain a noticeable quantity of free iodine, the turbidity rate of the mixture does not depend upon the iodine concentration, provided the alkali content is high enough. As we know, the reaction of acetone with iodine in an alkaline medium proceeds as follows [3]:

$$CH_3 \cdot CO \cdot CH_3 + 3I_2 + 3KOH = CH_3 \cdot CO \cdot CI_3 + 3KI + 3H_2O$$

$$CH_3 \cdot CO \cdot CI_3 + KOH = CH_3 \cdot COOK + CHI_3.$$

With equimolecular concentrations of all the components in the mixture, the velocity of this process ought to depend upon the concentration of each reagent. The chemical reaction of acetone with iodine in the presence of catalysts is a zero-order reaction with respect to iodine, however. In the presence of hydrogen ions, this peculiarity of the reaction was noticed long ago by Lapworth [4]. He found that the reaction rate was directly proportional to the concentration of acetone and of the hydrogen ions, but was independent of the concentration of iodine or other halogens.

According to contemporary notions, chemical reactions between non-ionic substances do not take place instantaneously. Only that small part of the total number of molecules that is active at the given instant can react; that is why the rate of the chemical transformation of a substance is proportional to the number of molecules in the corresponding activated state. This hypothesis makes it natural to conclude that substances taking part in slow reactions are present in two tautomeric forms.

It is usually thought that the acceleration of a reaction when catalysts are present is due to the catalysts' displacement of the equilibrium between the active and passive molecules toward the active forms; catalysts may lower the activation energy [5].

In the reactions of iodine with acetone, the active molecules of the latter are its enol form. Under normal circumstances, equilibrium between the keto and enol forms is established with a negligible percentage of the enol present. In the presence of catalysts (acids or alkalis), the equilibrium is shifted toward the enol form [6]. Various percentages of catalyst result in corresponding quantities of the enol. If negligible quantities of acetone are reacted with a large excess of iodine in the presence of an alkali, the concentration of iodine will be very high as against the enol. As a result, a change in the iodine concentration will not effect the reaction rate, i.e., the reaction will be of zero order with respect to the halogen.

Our chronometric turbidity method proved that this reaction was of the

foregoing nature: the turbidity rate does not depend upon the iodine concentration.

Naturally, at varying alkali concentrations we obtained varying absolute turbidity rates, as when this was so, the concentrations of the enol produced were not alike.

We found that the reaction was of zero order with respect to iodine in all mixtures with acetone, to which enough alkali was added to bleach all the iodine [1]. The picture is different when the amount of alkali present is inadequate. Then part of the iodine remains free. Under these conditions the turbidity rate of the reagent mixture is inversely proportional to the iodine concentration; the lower the iodine concentration, the faster the mixture grows turbid, [2].

At the time we put forward the following explanation for this peculiar phenomenon. When the percentage of alkali in the mixture is negligible (0.03%), the enol concentration will be very low. In any event, the enol concentration in such mixtures will be very much lower than the iodine concentration. This means that then the reaction will again be of zero order with respect to iodine, and, hence, the reaction rate (turbidity rate) cannot depend upon the iodine concentration. The free iodine (not bound by the alkali), however, can apparently dissolve the iodoform, and then the turbidity rate of the mixture will not reflect the reaction rate. Then the solubility of the iodoform will be a linear function of the concentration of free iodine. Thus, as the iodine concentration is reduced, the turbidity rate of the reagent mixture ought to rise.

In the present paper we furnish experimental proof of our foregoing hypothesis regarding the variation of the turbidity rate of alkaline mixtures of acetone and iodine with the concentration of free iodine. This likewise proves the zero order of this reaction with respect to iodine in the presence of the free halogen when the rate of the given reaction is investigated by means of our chronometric turbidity method.

EXPERIMENTAL

Direct determination of the solubility of iodoform in iodine solutions is quite difficult; we therefore took up the problem of whether iodine increases the solubility of iodoform in alcohol. We did this research by means of physicochemical titration with water until turbidity appears, using the method of S.I.Spiridonova [7]

When an alcoholic solution of iodiform is mixed with a large enough quantity of water, the solution grows turbid owing to the iodoform that separates out. If iodine can increase the solubility of iodoform in alcohol, introducing it into an alcoholic solution of iodoform will result in an increase in the amount of water that must be added to produce turbidity.

For our experiments, we prepared a 1% alcoholic solution of iodine (1 g of iodine per 100 ml of solution) and then diluted it with alcohol to produce a series of solutions with low iodine concentrations. Mixtures of 1 ml of the concentrated alcoholic solution of iodoform and 1 ml of iodine solution of a given concentration were prepared for titration with water. We prepared a mixture consisting of 1 ml of the foregoing iodoform solution and 1 ml of alcohol for use as a control. Three samples of each mixture were titrated. The average quantity of water required for titration was taken as the true value. The water was added from a microburette. The results of this test are given in Table 1.

If the iodine concentration in alcoholic solutions is plotted as the abscissa, and the volume of water added during titration as the ordinate, we get the ascending straight-line turbidity isotherm (cf figure).

As the figure shows, the volume of water used for titration rises with rising

TABLE 1

Titration of Alcoholic Mixtures of Iodoform and Iodine at Various Iodine Concentrations With Water (at 18°).

Iodine concentration, %	Quantity of water used in titration, ml			
	1st sample	2nd sample	3rd sample	Average value
0.000	0.204	0.206	0.196	0.202
0.0625	0.217	0.215	0.216	0.216
0.125	0.226	0.226	0.228	0.226
0.250	0.258	0.252	0.250	0.253
0.500	0.305	0.315	0.301	0.307
1.000	0.408	0.403	0.398	0.403

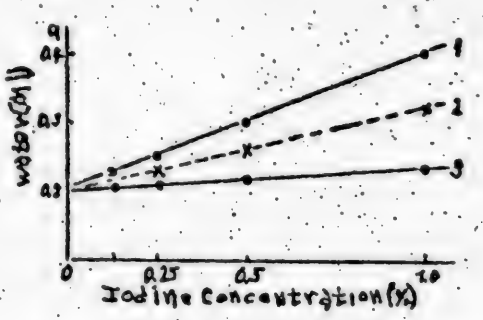

Fig. Titration with water of alcohol solutions of iodoform in the presence of iodine, potassium iodide, and alkali.

iodine concentration. This may be considered proof of the positive effect of iodine upon the solubility of iodoform; as the iodine concentration is raised, the solubility of the iodoform rises, and more water must be added to make the solutions turbid.

This conclusion is quite obvious for solutions containing free iodine. In the presence of substances that can react with iodine, even though partially, we must obtain a lower effect when the solutions are titrated with water in the presence of iodoform.

Iodoform itself does not enter into any chemical reaction with iodine, being the end product of iodination with a large excess of iodine. Such compounds as potassium iodide and an alkali, however, react actively with free iodine, lowering its concentration. Hence, in the presence of such substances, iodine exerts no noticeable influence upon the solubility of iodoform.

Table 2 gives the data on the titration of an alcoholic solution of iodoform in the presence of various quantities of iodine and potassium iodide. Alcoholic iodine solutions of varying concentration with twice the quantity of potassium iodide were added to the alcoholic solution of iodoform.

TABLE 2

Titration of Alcoholic Mixtures of Iodoform Iodine, and Potassium Iodide with Water (at 18°)

Iodine concentration, %	Quantity of water used in titration, ml			
	1st sample	2nd sample	3rd sample	Average value
0.000	0.200	0.201	0.198	0.200
0.0625	0.212	0.208	0.210	0.210
0.125	0.221	0.219	0.209	0.216
0.250	0.235	0.239	0.227	0.232
0.500	0.268	0.261	0.261	0.263
1.000	0.324	0.318	0.318	0.320

The turbidity isotherm of alcoholic solutions of iodoform when they are titrated with water in the presence of iodine and potassium iodide are shown by a dotted line in the figure. We prepared a 1:2 solution of a 1% alcoholic iodine solution and potassium iodide. Solutions with lower concentrations of the dissolved substances were prepared from this solution by diluting it with alcohol. Mixtures of 1 ml of each iodine solution with potassium iodide and 1 ml of the alcoholic iodoform solution were prepared for use in titration.

This new isotherm is also a straight-line curve, but its slope toward the axis of abscissas is smaller. It is easy to provide an explanation of this (nonparallel)

course of the isotherm. As the concentration of the iodine and the potassium iodide increases, the absolute quantity of the complex ion

$$I_2 + I' \rightleftarrows I_3'$$

formed rises. This naturally results in an increase in the loss of free iodine (its absolute quantity) and in a diminution of the volume of the water added for higher iodine concentrations.

If an alkali is added to an alcoholic solution of iodine and potassium iodide until the solution is decolorized, i.e., until all the free iodine is bound, the solubility of iodoform in such a mixture will be nearly independent of the concentration of the iodine used. This may be seen in the data for the titration with water of these mixtures, as shown in Table 3.

Table 3

Titration of Alcoholic Mixtures of Iodine and Iodoform with Water in the Presence of Potassium Iodide and Alkali (at 18°)

Iodine concentration, %	Quantity of water used in titration, ml			
	1st sample	2nd sample	3rd sample	Average value
0.000	0.195	0.205	0.203	0.201
0.125	0.210	0.208	0.199	0.206
0.250	0.210	0.210	0.210	0.210
0.500	0.215	0.217	0.216	0.216
1.000	0.235	0.235	0.230	0.233

The turbidity isotherm of these latter mixtures is likewise reproduced in our figure. It is a straight line, nearly parallel to the axis of abscissas.

It should be pointed out that the straight-line turbidity isotherm of alcoholic solutions of iodoform in the presence of free iodine may be employed to develop a method for the rapid determination of the concentration of alcoholic iodine solutions. This requires a control solution of iodine of fixed concentration. We can prepare another control solution by diluting such an alcoholic solution to twice its volume. A saturated alcoholic solution of iodoform may be employed as an indicator, which can produce turbidity when titrated with water. By determining the volume of water required to titrate the control and unknown solutions, we can compute the iodine concentration in the unknown solution by means of S.I.Spiridinova's equation [7]. In this case, the concentration must be computed from the equation:

$$x = \frac{c}{1 + \frac{a - a_1}{a_2 - a_1}},$$

where c is the concentration of the iodine solution, and a_1, a_2, and a are the volumes of water used to titrate control solutions I and II and the unknown solution, respectively. This method may be easily employed to determine iodine concentration when a titrated solution of sodium thiosulfate is unavailable. The most convenient concentration of the control iodine solution is one that does not exceed 0.5%.

SUMMARY

1. It has been found experimentally that the solubility of iodoform is increased when free iodine is present.

2. An explanation is given for the fact that the turbidity rate of alkaline mixtures of acetone and iodine is inversely proportional to the iodine concentration. This is not due to the total quantity of iodine present, but solely to the concentration of the free halogen. The true rate of formation of iodoform in the reagent mixture does not depend upon the concentration of the iodine used for the reaction.

3. Straight-line turbidity isotherms have been obtained for alcoholic solutions of iodoform in the presence of varying quantities of iodine during titration with

water; this shows that the solubility of the iodoform is a linear function of the iodine concentration.

4. The feasibility of rapid determination of the percentage of iodine in its alcoholic solutions by means of titrating the solution with water until turbidity sets in, with iodoform present as an indicator, is pointed out.

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Received August 1, 1947.

THE REACTION OF POTASSIUM CHLOROPLATINATE WITH ISOMERIC AMINOBENZOIC ACIDS

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In connection with our previously published research [1] on the coordination compounds of platinum with aliphatic amino acids, we were interested in also exploring the derivatives of amino acids, chiefly, the ortho, para, and meta aminobenzoic acids. On the basis of Chugayev's ring rule it was to have been expected that only the ortho acid could yield a "claw-shaped" derivative, containing a six-membered ring.

The corresponding derivatives of the meta and para acids must contain seven- and eight-membered rings, and for this very reason it is hardly likely that they can exist. That is why, when these acids react with K_2PtCl_4, we may expect them to exhibit a coordination capacity of one, combined with the metal via the amino group.

But even the ortho acid, which can give rise to a closed cycle, according to the ring rule, has properties that differ from those of aliphatic amino acids. According to Bjerrum [2], these latter amino acids exist in aqueous solution as amphoteric ions of the $\begin{matrix}CH_2NH_3^+\\ |\\ COO^-\end{matrix}$ type. Moreover, aromatic amino acids exhibit much less of a tendency to form such amphoteric ions, which leads one to think that they also have much less of a tendency to form cyclic groupings with metals than their aliphatic analogues.

In the light of the above, one might think that the reaction of ortho aminobenzoic acid with K_2PtCl_4 also ought to yield both claw-shaped derivatives and analogs of the derivatives of the meta and para acids. The experimental data cited below have fully borne out these theoretical assumptions.

EXPERIMENTAL

Reaction of K_2PtCl_4 with o-Aminobenzoic (Anthranilic) Acid

A solution of 1.32 g of o-aminobenzoic acid in 100 ml of water was added to a solution of 1 g of K_2PtCl_4 in 10 ml of water (on the basis of 4 mols of acid per mol of the platinite). The reaction was carried out by heating over a water bath while allowing a current of CO_2 to pass through. It was found advisable to begin heating only after the solutions had been mixed in order to avoid the production of oxidation products. The solution retained the color of the platinite for some time, after which it began to grow paler; an almost insoluble, finely crystalline, yellowish precipitate began to settle out after heating had gone on for half an hour. Sometimes the product had a greenish tinge, at others a grayish tinge. When no CO_2 was passed through, the precipitate had a more intense color, purplish deposits then settling out secondarily.

In view of this circumstance, we did our work in a current of CO_2. The solution, cooled in a current of CO_2, was drawn off from the precipitate, and the precipitate was dried in a vacuum exsiccator over H_2SO_4 until its weight remained constant. The product yield amounted to about 1 gram; the filtrate was colorless at first, but turned purple upon standing; this color change was particularly rapid when it was exposed to sunlight.

The product, dried to constant weight, was analyzed to establish its platinum and chlorine content, and it was also titrated with 0.1 N alkali in the cold in the presence of phenolphthalein. Preliminary tests indicated that the product exhibited the properties of an acid.

Analyses for platinum and chlorine and the titration yielded the following results:

First preparation: %: Pt 35.53, 36.06; Cl 10.38.
Second preparation: %: Pt 36.63, 37.19, 36.95; Cl 10.46, 10.31, 10.69; H^+ 0.26, 0.31, 0.26.
Third preparation: %: Pt 37.52; Cl 10.32; H^+ 0.27.
$[PtCl_2(NH_2C_6H_4COOH)_2]$. Calculated %: Pt 36.18; Cl 13.14; H^+ 0.37.

As for the cyclic compound with the composition $[Pt(NH_2C_6H_4COO)_2]$, it must neither contain any chlorine nor be titratable against hydrogen.

The analytical data cited, together with the picture yielded by microscopic observation, indicate that we are dealing with a mixture of two substances: We assumed that the compounds entering into the mixture were $[PtCl_2(NH_2C_6H_4COOH)_2]$ and $[Pt(NH_2C_6H_4COO)_2]$. If this is really the case, the quantity of $[PtCl_2(NH_2C_6H_4COOH)$ component in the mixture may be found from the titration of chlorine-determination data. The ratio of the chlorine to the titrating H^+ must equal unity.

We cite herewith data for a computation of this sort: 0.1866 g of the preparation was used in titration. During titration most of the substance entered solution. Part of the substance (gray in color) remained undissolved; it was filtered out and weighed, totalling 0.0391 g. Assuming that the titrating portion is $[PtCl_2(NH_2C_6H_4COOH)_2]$, whereas the insoluble portion is $[Pt(NH_2C_6H_4COO)_2]$, we can calculate the analysis data. In the given case, the weight of the undissolved portion was approximately 21% of the initial batch. Assuming that the initial batch consists of 21% $[Pt(NH_2C_6H_4COO)_2]$ and 79% $[PtCl_2(NH_2C_6H_4COOH)_2]$, it is readily found that the preparation must contain 37.33% Pt and 10.39% Cl.

These figures are quite close to those found directly in our experiment, which indicates that under the specified conditions the composition of the mixture fluctuates within rather narrow limits.

These results led us to make an endeavor to separate the components of the mixture by treatment with an alkali.

Separation of the Mixture Components

This operation was performed as follows: a weighed batch of the initial mixture was titrated with a solution of potassium hydroxide in the cold in the presence of phenolphthalein. The alkali was added in small portions with constant stirring. The undissolved fraction was filtered out, washed with water, and dried in a drying chamber at 100°. The thus-treated preparation of the undissolved fraction was analyzed to determine its platinum and nitrogen content. At the same time, a qualitative determination was made of its chlorine and titratable hydrogen.

Experiment showed that preparations of this sort contain only traces of chlorine and are not titrated against alkali.

Analysis of the various preparations of the undissolved fraction yielded the following results:

Found %: Pt 41.86, 41.44; N 6.54.
$Pt(NH_2C_6H_4COO)_2$. Calculated %: Pt 41.79; N 5.99.

The filtrate left after removal of the $Pt(NH_2C_6H_4COO)_2$ salt was treated with concentrated hydrochloric acid, causing a yellowish precipitate to settle out. The precipitate was drawn off, washed with water and alcohol, and dried, first in an exsiccator over H_2SO_4 and then in a drying chamber with the temperature gradually raised to 100°.

Found %: Pt 36.75, 36.66, 36.49; Cl 12.37, 12.49, 12.24, 12.87.
$[PtCl_2(NH_2C_6H_4COOH)_2]$. Calculated %: Pt 36.15; Cl 13.14.

The foregoing method makes possible the almost complete separation of the components of the initial mixture.

Action of m-Aminobenzoic Acid on K_2PtCl_4

A solution of 0.66 g of m-aminobenzoic acid in 30 ml of water was added to a solution of 0.5 g of K_2PtCl_4 in 10 ml of water, heated over a water bath (4 mols of acid per mol of K_2PtCl_4, as in the previous instance).

The reaction was carried out by heating over a water bath while a current of CO_2 was passed through. After a few minutes had elapsed, the solution lost its color and turned yellowish, a yellowish, finely crystalline, almost insoluble precipitate being thrown down. The precipitate was drawn off, washed with water and alcohol, and dried in a drying chamber whose temperature was gradually raised to 100°.

The substance possesses acid properties and can be titrated with alkali in the presence of phenolphthalein.

Analysis yielded the following results:

Found %: Pt 36.06, 35.94, 35.80; Cl 12.41, 12.55, 12.31; H^+ 0.34.
$[PtCl_2(NH_2C_6H_4COOH)_2]$. Calculated %: Pt 36.15; Cl 13.14; H^+ 0.37.

An arresting circumstance is that the chlorine figures are somewhat below the theoretical values, evidently because of the presence of small quantities of impurities that contain no chlorine. Nonetheless, in this case the synthesis conditions yielded a more homogeneous substance than was the case with the ortho acid.

Action of p-Aminobenzoic Acid on K_2PtCl_4

The reaction was carried out under the same conditions as those used for the ortho acid. In this case, the product is formed extremely rapidly. It is a light-yellow, finely crystalline substance.

The drawn-off precipitate was carefully washed with water and, particularly, alcohol to remove traces of p-aminobenzoic acid. After the substance had been brought to constant weight in a drying chamber, it was analyzed for Pt, Cl, and H^+.

Found %: Pt 35.98, 35.71, 35.97, 35.50, 35.93; Cl 13.03, 13.03, 12.81, 12,89, 12.95; H^+ 0.39, 0.40, 0.40, 0.40.
$PtCl_2(NH_2C_6H_4COOH)_2$. Calculated %: Pt 36.15; Cl 13.14; H^+ 0.37.

In this case the synthesis product is a preparation that is contaminated only with traces of the para acid, which are removed by alcohol.

Action of Thiourea on the Product of Combining Platinum Chloride with p-Aminobenzoic Acid

$PtCl_2(NH_2C_6H_4COOH)_2$ was reacted with thiourea in order to ascertain its configuration.

Our attempt to dissolve the compound in an aqueous solution of thiourea under the usual mild reaction conditions failed because of its extremely low solubility and the extremely low rate at which it passed into solution.

We therefore proceeded as follows: a weighed batch of the substance was dissolved by titrating it with alkali, and concentrated solutions of thiourea were reacted with the solution produced. Careful heating over a water bath, with constant stirring, brought about the rapid precipitation of a yellow, crystalline deposit. The drawn-off and dried precipitate exhibited a platinum constant that was close to what is required for a tetrathiourea derivative.

Found %: Pt 33.80.
$[Pt(Thio)_4]Cl_2$. Calculated %: Pt 34.24.

This result supports the conclusion that the compound we have newly synthesized behaves like a cis derivative.

$$\begin{bmatrix} Cl & & NH_2C_6H_4COOH \\ & Pt & \\ Cl & & NH_2C_6H_4COOH \end{bmatrix}$$

The Splitting off of CO_2 from $PtCl_2(NH_2C_6H_4COOH)_2$ Compounds

Sultanov [3] has described the splitting off of CO_2 from various carboxylic acids. The acids investigated by him included the isomaeric aminobenzoic acids. He showed that when ortho aminobenzoic acid was heated to from 145 to 205°, CO_2 was given off. The same phenomenon was observed with the para isomer (temperature of CO_2 evolution 187°).

Under these same conditions m-aminobenzoic acid does not exhibit the liberation of CO_2. We decided to explore the behavior of our complex derivatives of three isomeric aminobenzoic acids in this respect. The experiments were carried out as follows: a sample of the coordination compound was placed in a test tube, which was sealed with a stopper and fitted with two branch tubes. The test tube was connected to a U-tube that contained freshly prepared, completely transparent baryta water. Air that had been freed of its carbon dioxide by first passing it through several Tishchenko bottles containing a strong alkali was drawn through the system. The test tube containing the substance to be tested was placed in an oil bath and gradually heated. A thermometer was immersed in the oil bath. At first, Sultanov's experiments with free amino acids were repeated. We actually observed the splitting off of carbon dioxide from ortho and para aminobenzoic acids, but did not observe this happening with the meta isomer.

Our sole deviation from Sultanov's data consisted in the decomposition of the ortho acid occurring at 230-240° in our experiments, and that of the para acid occurring at 215°. The most likely explanation for this discrepancy is the difference in the heating methods employed. After having thus corroborated Sultanov's findings, we set up our experiment with the coordination compounds.

It turned out that the coordination compounds of the ortho and meta acids behaved like the free acids. In particular, the ortho coordination compound exhibited an abundant liberation of CO_2 at 230-240°, while the meta coordination compound exhibited no evolution of CO_2. As for the para derivative, the properties of the free, uncoordinated acid differed from those of the coordination compound. Whereas the free acid undergoes decomposition with the evolution of CO_2, the coordination

compound does not exhibit this phenomenon, even when heated to a fairly high temperature.

The test tubes contained a grayish-black residue after the thermal decomposition of the coordination compounds. The ortho coordination compound, which decomposed with the evolution of carbon dioxide, ought to have yielded a coordination compound containing aniline. Under the prevailing conditions of our experiments, however, oxidation by atmospheric oxygen could have taken place.

We propose to perform experiments on the thermal decomposition of the ortho coordination compound in an atmosphere of an inert gas, in order to obtain and study an unchanged reaction product.

SUMMARY

It has been established that the aromatic amino acids yield coordination compounds in which they occupy only one coordination position via the amino group. Only in the case of the ortho isomer is there a partial formation of a cyclic derivative.

We synthesized three isomeric compounds of the following composition:

$$PtCl_2(NH_2C_6H_4COOH)_2.$$

Their isomerism is due to the isomerism of the coordination substituents. For the derivative of the para acid, a reaction with thiourea indicated the cis configuration of the synthesized compound.

Thus, the isomeric aminobenzoic acids, like their addition compounds, behave like amines.

Endeavors to synthesize isomers of trans configuration are under way at the present time, as well as certain physico-chemical measurements.

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Received November 15, 1948.

THE EFFECT OF ADDING ORGANIC COMPOUNDS UPON THE VELOCITY OF THE SOAPMAKING PROCESS

I. EFFECT OF ADDING AROMATIC HYDROXY COMPOUNDS UPON THE VELOCITY OF THE SAPONIFICATION OF COTTONSEED OIL BY POTASSIUM HYDROXIDE (ACTION OF PHENOL)

B. A. Rashkovan and V. M. Lebedeva

As we know, the addition of organic compounds is common practice in the technology of soap manufacture. Most often, these additives are intended to confer special properties upon the soap (disinfecting, washing off oils, etc.).

Some organic substances, when added to a fatty mixture, change the velocity of the saponification process.

The literature contains references to the catalytic action of various organic compounds upon the velocity of the saponification of fats and oils. Rozhdestvensky [1], for example, observed that the addition of some phenols, especially those that that are only slightly soluble in water, such as cresol, the naphthols, and thymol, accelerates the saponification of oils. In agreement with Langmuir's and Harkins' views, Rozhdestvensky [1] ascribed the action of the phenols to an increase in the number of ether-glyceride bonds at the surface separation.

Smith [2] likewise commented on the catalytic effect of some organic compounds – the naphthols, ethyl alcohol, fatty acids oxidized cod-liver oil – on the saponification rate of oils by the "cold" process, but he rejected Rozhdestvensky's viewpoint, given above, on the reason for the phenol's catalytic action. He did not offer any other explanation, however.

In our opinion, the catalytic action of the phenols and other organic compounds may be ascribed to several causes:

1) An increase in the dispersion of the oil.

2) Some change in the mechanism of the saponification process.

3) A direct transition from the stage of emulsion saponification to that of rapid saponification, avoiding the process of retarded saponification.

We employ the stage nomenclature proposed by one of the present authors previously, [3].

As we see it, the catalytic action of a phenol is essentially an increase in the degree of dispersion of the emulsion and the formation of phenolates, which dissolve in the soap and participate in the saponification process. The high dispersion of the emulsion tends to accelerate the penetration of the oil and the alkali into the soap layer.

When enough soap is present, this results in the water-oil emulsion passing directly into the system of oil and water in the soap. In the absence of a catalyst and with low dispersion, the emulsion is first broken down, after which a new system is formed [3]. This causes a marked retardation of the rate of saponification. The presence of such systems and the changes in the system's phases have been

proved by us experimentally.

We consider that the saponification of fats takes place in the soap, assuming the following mechanism for the process.

The oil dissolves in the soap micelles, namely, in the hydrocarbon chains, as takes place, according to P.A.Rebinder [4], with hydrocarbons in the formation of superstructures.

Phenolates also dissolve in hydrated soap, undergoing hydrolysis in it and forming the alkali required for saponification. The hydrolysis of the phenolates in the soap is all the greater in that the alkali formed as the result of this hydrolysis is consumed in saponifying the oil, whereas the soap readily absorbs water and is easily hydrated. Thus, the phenol acts as an alkali carrier, whose solubility in soap is considerably lower than in phenolates. As we use concentrated alkali solutions in saponification, the conditions prevailing in the system favor the phenol's being able to play its part directly. The hydrolysis of the phenolates may be ignored in these alkali solutions. The literature contains references to the feasibility of using phenolates in saponifying esters. Smith [5] employed potassium cresylate to saponify ethyl acetate in aqueous alcoholic solutions.

The notion of the mechanism of catalytic action set forth by us above is supported by a study of the variation of the catalytic action of hydroxy compounds with the ratio between the hydrocarbon part of the molecule, which governs solubility in soap, and the hydroxy groups, which increase solubility in water. As we know, this ratio, together with other factors, also has a great effect upon the surface activity of these compounds at the water-oil interphase boundary and, hence, upon the degree of dispersion of the emulsion.

EXPERIMENTAL

In accordance with what has been stated above, we investigated the influence of adding chemically pure phenol upon the reaction rate of the saponification of cottonseed oil by solutions of potassium hydroxide. The cottonseed oil we used in these experiments was first carefully refined by us. The potassium hydroxide was a chemically pure preparation.

It was found that the presence of a small percentage of carbonates in the potassium hydroxide has absolutely no effect upon the reaction rate. McBain [6] made the same observation in the saponification of fats by solutions of sodium hydroxide containing traces of carbonates.

The experiments were set up as follows: a weighed batch of cottonseed oil, between 100 and 200 g, was placed in the reaction vessel, and the organic compound was added. The vessel was placed in a thermostat, and its contents were carefully mixed together by means of a stirrer. The alkali was first heated in the same thermostat. When the liquid had been warmed up to the thermostat temperature, the alkali was quickly added to the oil, with vigorous stirring.

Beginning at the instant the reagents were mixed together, samples of the mixture were taken at fixed intervals of time and transferred to previously weighed boxes containing 20% hydrochloric acid. The percentage of oil saponified was determined by titrating the free fatty acids, as described by us in an earlier report [3].

The cottonseed oil was saponified with a 51% solution of potassium hydroxide at various temperatures. The variation of the phenol's catalytic action with its concentration was determined. Addition of phenol produces an appreciable acceleration of the saponification reaction. This acceleration is especially marked at the start

of the reaction, approximately for an hour after the reagents have been mixed together.

The action of phenol is evident when we examine Fig. 1, in which the isotherm curves are plotted for the saponification of cottonseed oil with a 51% solution of potassium hydroxide at a temperature of 60° in the presence of phenol (Curve 1) and without any phenol present (Curve 2).

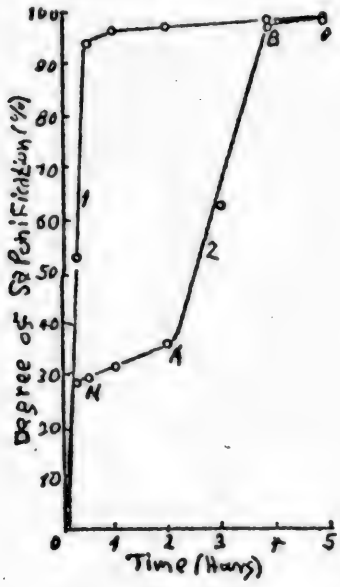

Fig. 1. Effect of adding phenol upon the reaction rate of saponifying cottonseed oil with potassium hydroxide at 60°.

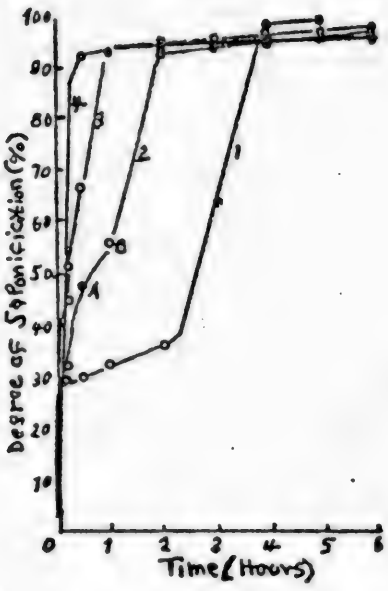

Fig. 2. Effect of phenol concentration upon the rate of saponification at 60°.

Comparison of the curves shows that the addition of phenol produces an extremely sharp acceleration of the process at the start (13%/minute as against 0.99); later on there is but little change in the process rate; during the interval from half an hour to 6 hours only 5% of the oil is saponified.

Comparison of the process rate along the various sections of Curve 2 with that along the corresponding sections of Curve 1 indicates that when phenol is present the section corresponding to the stages of retarded saponification is eliminated. Along the other sections of the curve, with the exception of the post-saponification stage, the reaction rate is much greater than when no phenol is present.

The elimination of the stage of retarded saponification can be explained by the considerations we have set forth above, as well as by the fact that the phenol greatly increases the stability of the emulsion. This is also borne out by the outward appearance of the system, which is completely stratified (3) at temperatures above 60° when no phenol is present, no stratification occurring when phenol is added.

The effect of phenol concentration upon its catalytic action at 60° is shown in Fig. 2.

The shape of the curves in Fig. 2 indicates that at phenol concentrations of 0.06 (2) and 0.125 (3) there is a certain bend in the curves (section AB), corresponding to a slight retardation of the saponification process. This bend straightens

out at higher phenol concentrations (0.250, 0.500, and 1.000 g). This agrees completely with the effect of an increase in the phenol concentration upon the stability of the emulsion and, accordingly, upon the length of the period of retarded saponification. Fig. 2 likewise shows that increasing the phenol concentration, up to a certain limit, increases the rate at which the oil is saponified.

According to what has just been said, all the factors tending to increase the emulsion's stability reduce the period of retarded saponification and thus tend to accelerate the process of saponification during its initial stage and to facilitate the conversion of the water-oil emulsion into a system of oil and water in the soap.

The same factors that reduce the stability of the emulsion slow down the rate at which emulsion saponification takes place, thus resulting in the appearance of the stage of retarded saponification and the prolongation of the latter. That is why temperature exerts an important influence upon the velocity of the process. In general, the effect of temperature is to affect the stability of the emulsion and the viscosity. As we know, raising the temperature lowers the stability of the emulsion and also lowers the viscosity of the system; hence, we may expect that raising the temperature ought to slow down the rate of emulsion saponification, bring about the stage of retarded saponification, and increase the reaction rate in the post-saponification stage.

The results of tests made by us at various temperatures confirm the correctness of these conclusions.

Fig. 3, in which there are plotted the curves of change in the rate of saponification at temperatures of 40 and 80° with phenol present or absent during saponification with a 56% solution of potassium hydroxide, shows this clearly. To avoid the curves' running together, the origin has been shifted somewhat along the axis of abscissas for Curves 3 and 4. The form of the curves indicates a reduction in the rate of emulsion saponification at 80° compared to that at 40°, and a considerable increase in the duration of the stage of retarded saponification, which is as long as several hours at 80°, but only 15 minutes (section AB) at 40°.

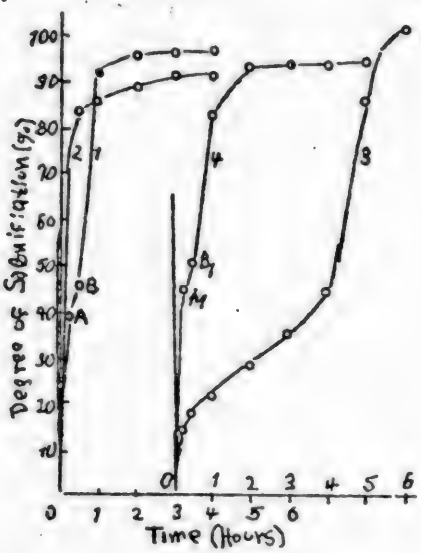

Fig. 3. Effect of temperature on rate of saponification.

1 – 40° with no phenol present;
2 – 40° with phenol;
3 – 80° with no phenol present;
4 – 80° with phenol present.

SUMMARY

1. A study has been made of the effect of the addition of phenol upon the rate of saponification of cottonseed oil by concentrated solutions of potassium hydroxide.

2. It is shown that phenol accelerates the rate of emulsion saponification and facilitates the direct transition from emulsion saponification to rapid saponification.

3. The influence of the phenol concentration and of the temperature upon the various stages of soap manufacture has

been elucidated.

4. An explanation is suggested for the "catalytic" action of phenol upon the rate of saponification and soap making.

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Received December 3, 1947.

THE EFFECT OF ADDING ORGANIC COMPOUNDS UPON THE VELOCITY OF THE SOAPMAKING PROCESS

II. THE CATALYTIC ACTION OF AROMATIC HYDROXY COMPOUNDS UPON THE VELOCITY OF THE SOAPMAKING PROCESS

B. A. Rashkovan and V. M. Lebedeva

The Effect of Adding Naphthol Upon the Rate of Saponification of Cottonseed Oil

The catalytic action of naphthol in the saponification of fats was established by Rozhdestvensky [1] and confirmed by Smith [2].

Our data on the effect of adding naphthol upon the rate of saponification of cottonseed oil are given in Fig. 1. The graph shows the isotherm curves for the saponification of cottonseed oil by a 56% solution of potassium hydroxide at 60° in the presence of 0.120 g of napthol (Curve 2) and 0.750 g of naphthol (Curve 3).

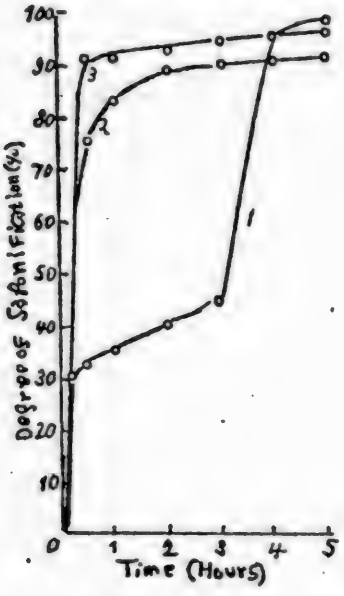

Fig. 1. Effect of naphthol concentration upon the rate of saponification of cottonseed oil.

Curve 1 is the isotherm for the saponification reaction at the above conditions but with no naphthol present.

Comparison of these curves indicates that adding naphthol has an effect like that of adding phenol, i.e., it accelerates the reaction; moreover, as in the case of phenol, this acceleration is largely manifested during the initial period of the saponification reaction, especially during the interval that corresponds to the stage of emulsion saponification; the stage of retarded saponification is eliminated. The variation with temperature and concentration is, on the whole, the same for naphthol as for phenol. Naturally, the considerations cited above in connection with the action of phenol may be applied in toto to explain the "catalytic" action of naphthol.

Naphthol has a greater catalytic action than phenol, however. This is readily explained by the higher solubility of the naphtholates in soap and by naphthol's higher surface activity at the water-oil interphase boundary.

The Effect of Adding Hydroquinone, Resorcinol, Pyrocatechol, and Pyrogalliol Upon the Rate of Saponification of Cottonseed Oil

An altogether different picture presents itself when we explore the effect of

adding hydroquinone and pyrogallol upon the rate of saponification of cottonseed oil. Not only do additions of these substances not accelerate the process of emulsion saponification, but, on the contrary, they retard it considerably. This is borne out by Fig. 2, in which there are plotted comparative curves for the change in the saponification rate with time and with the addition of these substances.

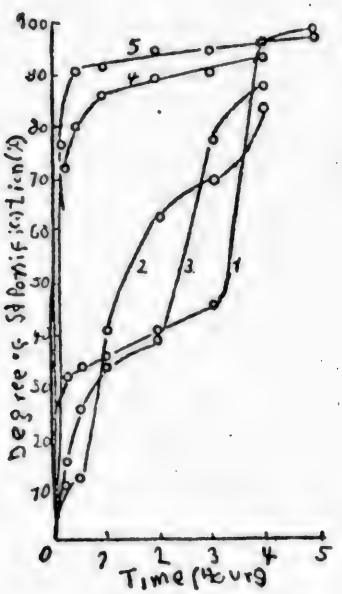

Fig. 2. Effect of adding aromatic hydroxy compounds upon the rate of saponification of cottonseed oil.

There are five curves plotted in Fig. 2: Curve 3 is the 60° isotherm for the rate of saponification of cottonseed oil by a 56% solution of potassium hydroxide; Curves 2, 4, and 5 are the corresponding isotherms when pyrogallol, phenol, and naphthol are present, respectively, while the other conditions remain the same. Curve 1 is the isotherm when no additive is present. The effect of the addition of hydroquinone upon the individual stages of the process is seen in the tabular

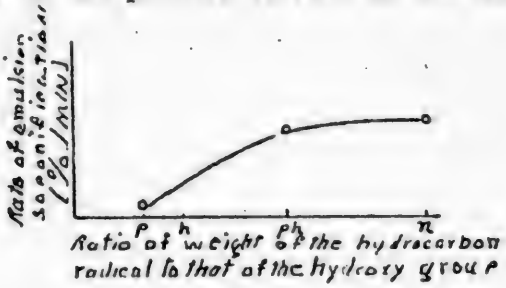

Fig. 3. Rise in the catalytic action of aromatic hydroxy compounds with the accumulation of hydroxy groups within the molecule.

data. The action of pyrogallol is more complicated; as we know, this latter oxidizes very easily and, thus, the effect of its oxidation products begins to make itself felt soon after it is mixed with the alkali; this explains the abnormal shape of the pyrogallol curve.

The effects of resorcinol and pyrocatechol upon the saponification are like that of hydroquinone. These compounds produce an even greater change in the rate of emulsion saponification than that effected by hydroquinone.

The subjoined table and Fig. 3 show that an accumulation of hydroxy groups in the molecule of an aromatic compound lowers its catalytic action during the stage of emulsion saponification, even resulting in negative catalysis; raising the molecular weight by increasing the size of the radical increases the catalytic action of hydroxy compounds during this stage.

The Effect of Adding Hydroquinone Upon the Rate of Saponification by Stages

	Process velocity, per cent/minute		
	Stages		
	Emulsion saponification	Retarded saponification	Accelerated saponification
Without hydroquinone...	1.1	0.07	0.83
With hydroquinone present.....	0.73	0.13	0.63

Figure 3 clearly shows the rise in the catalytic effect of aromatic hydroxy compounds during the emulsion stage of saponification as a function of the accumulation

of hydroxy groups in the molecule and of the weight of the radical. The points p, h, ph, and n denote the numerical values of the ratio of the weight of the radical to that of the hydroxy groups for pyrogallol, hydroquinone, phenol, and naphthol, respectively. Figure 3 makes it clear that as the ratio of the weight of the hydrocarbon radical to that of the hydroxy groups in the molecule rises, the catalytic action increases.

The dissimilarities in the catalytic action of the various compounds is due to their different surface activities at the interface boundary: oil – concentrated alkali solution. We made an experimental determination of the surface tension at the oil – concentrated alkali solution boundary surface when 1% of phenol or an equimolecular quantity of the above-mentioned compounds was present. The surface tensions were found to be 0.25 dyne/cm for naphthol, 8.03 for phenol, 34.89 for hydroquinone, and 31.2 for resorcinol.

The foregoing confirms the mechanism for the catalytic action of these compounds proposed above.

SUMMARY

1. The effect of adding aromatic hydroxy compounds upon the rate of saponification of cottonseed oil by potassium hydroxide has been investigated.

2. It has been shown that naphthol possesses a greater "catalytic" action than phenol. An explanation is furnished for the so-called "catalytic" action of naphthol.

3. Hydroquinone and pyrogallol slow down the rate of emulsion saponification.

4. As hydroxy groups accumulate in the molecule of an aromatic compound, its catalytic action is diminished.

5. The catalytic action of hydroxy compounds in the emulsion stage of saponification increases with a diminution of the surface activity of these compounds at the oil-concentrated alkali solution interphase boundary.

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Received December 3, 1947.

THE EFFECT OF ADDING ORGANIC COMPOUNDS UPON THE VELOCITY OF THE SOAPMAKING PROCESS

III. THE CATALYTIC ACTION OF ALIPHATIC ALCOHOLS AND ALDEHYDES UPON THE VELOCITY OF THE SOAPMAKING PROCESS

B. A. Rashkovan and V. M. Lebedeva

There are references in the literature to the catalytic action of ethyl alcohol upon the saponification process [1]. Smith explains the catalytic action of alcohol as being due to the fact that when even a slight quantity of alcohol is present, the saponification reaction takes place in a homogeneous alcoholic solution of the oil and the alkali. He bases this explanation upon the concept of the higher solubility of alcohol in the soap, as compared to water. As there is little soap present at the beginning of the reaction, it is saturated with alcohol. Soap thus saturated with alcohol acts as a solvent for the fats and alkali. Experiments we have carried out on the catalytic action of alcohols indicate that in this case the principal factors at work are the same as those acting in the hydroxy compounds of the aromatic series, especially, the reduction of the surface tension at the oil – concentrated alkali solution interphase boundary and the rise in the dispersion and stability of the emulsion. We measured the surface tension at this interphase boundary experimentally; it was found to be 22.62 dyne/cm when 0.5% of ethyl alcohol was used, and 8.27 and 4.96 dyne/cm, respectively, with equimolecular quantities of butyl and isoamyl alcohols.

Microscopic analysis indicated that most of the drops have diameters up to 2μ at 25° when these alcohols are present; when the other conditions were the same but no alcohol was added, the diameters of most of the drops exceeded 10μ. This, to be sure, does not exclude the possibility of also treating the role of the alcohol as a factor that increases the solubility of the alkali in the soap.

We investigated the effect of ethyl, butyl, and isoamyl alcohols upon the saponification rate of cottonseed oil.

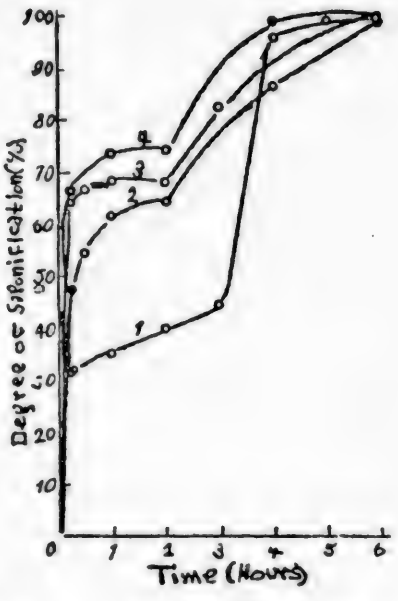

Fig. 1. Variation in the rate of saponification of cottonseed oil by potassium hydroxide in the presence of alcohols.

The effect of small additions of alcohol are clearly evident in Fig. 1. This graph contains 4 curves showing the change in the rate of saponification of cottonseed oil with time when no alcohol is present, (Curve 1), and in the presence of small amounts of ethyl alcohol (Curve 2), butyl alcohol (Curve 3),

and isoamyl alcohol (Curve 4).

Comparison of these curves shows that when a small quantity of any of these alcohols is present, the reaction rate rises during the initial period, though not to the same extent.

TABLE 1

Change in the rate of Emulsion Saponification in the Presence of Various Alcohols

Alcohol	Rate of emulsion saponification, per cent/minute	Ratio of weight of the hydrocarbon radical to that of the hydroxyl group
Ethyl	1.83	1.71
Butyl	2.23	3.35
Isoamyl	2.31	4.18

TABLE 2

Change in the Rate of Accelerated Saponification in the Presence of Various Alcohols

Alcohol	Rate of Emulsion saponification, per cent/min.	Ratio of weight of the hydrocarbon radical to that of the hydroxyl group
Ethyl	0.18	1.71
Butyl	0.20	3.35
Isoamyl	0.21	4.18

As in the aromatic hydroxy compounds, the reaction rate during the emulsion stage of saponification depends on the ratio of the weight of the hydrocarbon radical to that of the hydroxy groups in the molecule; as this ratio increases, the rate of emulsion saponification rises. It was stated above that this is due to an increase in the surface activity of the alcohols at the oil – concentrated alkali solution interphase boundary.

Increasing the concentration of alcohol raises its catalytic effect, up to a certain limit. Each alcohol has an optimum concentration at which the rate of emulsion saponification is a maximum, with the duration of the stage of retarded saponification reaching a minimum and even disappearing completely. The addition of 0.4% of ethyl alcohol results in shortening the length of the stage of retarded saponification from 2.5 hours to 1 hour. Increasing the quantity of added alcohol to 1% results in the complete elimination of the stage of retarded saponification; emulsion saponification passes directly into rapid saponification. Further increase in the concentration of alcohol, however, again causes an inflection to reappear in the curve, though it is not a very sharp one. The same relationships are found for butyl and isoamyl alcohols, but they are much more sharply marked.

TABLE 3

Effect of Temperature Upon the Rates of Emulsion and Accelerated Saponification of Cottonseed Oil in the Presence of Butyl Alcohol.

Process Stage	Rate of process (per cent/min) at various temps.		
	40°	60°	100°
Emulsion saponification	1.37	2.07	0.67
Accelerated saponification	0.19	0.20	0.54

Table 2 indicates the change in the process rate during the stage of accelerated saponification when the alcohols mentioned above are present.

An increase in temperature, involving a reduction in the degree of dispersion and in the stability of the emulsion, reduces the process rate during the emulsion stage of saponification accordingly; there is, however, an optimum temperature for the rate at which this process takes place, at which the stability and the dispersion of the emulsion are sufficiently high, while the coefficient of the reaction rate rises with the temperature. For the alcohols discussed here the optimum temp-

erature under our experimental conditions is 60°.

The effect of temperature upon the rate of emulsion and accelerated saponification is shown in Table 3.

The same relationships exist in the post-saponification stage as in accelerated saponification, but they are not nearly as prominent.

Effect of Adding Aldehydes Upon the Rate of Saponification of Cottonseed Oil by Alkalies

We have found no research paper in the literature on the catalytic action of aldehyde and ketones upon the saponification of fats and oils. We investigated the effect of formaldehyde and acetaldehyde upon this process. The experimental results indicated that both formaldehyde and acetaldehyde are catalytsts of the saponification reaction. The catalytic action of the aldehydes resembles that of phenol and naphthol. Like these latter compounds, they produce a marked acceleration of the soap-making process at the very start; the stage of retarded saponification is entirely eliminated, and the process of emulsion saponification passes directly into the stage of accelerated saponification. When the aldehyde concentration is high enough, the curve of the saponification process seems to consist of two branches: an abrupt rise, corresponding to the stages of emulsion and accelerated saponification, followed by a bend in the curve – the stage of final saponification.

TABLE 4

Time, hours	Degree of saponification, per cent, at various additions of acetaldehyde per 100 g of oil		
	0.7 g	1.4 g	2.8 g
0.25	61.0	64.5	–
0.5	81.8	70.9	66.4
1.0	86.3	–	88.1
2.0	–	90.0	89.9
3.0	90.2	92.7	92.3
4.0	91.5	94.3	94.1
5.0	95.5	94.9	–

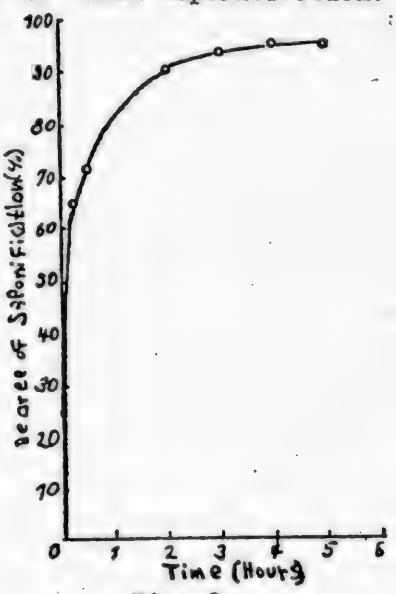

Fig. 2.

The data of Table 4 show that even at an acetaldehyde content of 0.7% its catalytic action is very striking. Raising the acetaldehyde concentration increases its catalytic action. But as was the case with the alcohols, when a certain concentration is reached, there is an inflection in the curve, corresponding to the stage of retarded saponification. Thus, at certain concentrations the behavior of acetaldehyde resembles the action of ethyl alcchol. With 1.4 g of acetaldehyde present per 100 g of oil, its catalytic action at 40° is most marked. Figure 2 shows the curve of the saponification of cottonseed oil at this concentration and under the experimental conditions sepcified above. The high viscosity of the system retards the reaction rate of this process during the post-saponification stage.

Raising the temperature lowers the rate of emulsion saponification, as clearly seen in Fig. 3.

As the temperature is raised, the rate of the soap-making process increases somewhat in the ensuing stages, however. At bottom, the effect of temperature is

manifested in its affecting the dispersion of the emulsion and the viscosity and stability of the system. The action of formaldehyde is like that of acetaldehyde, but less marked. The catalytic action of formaldehyde is shown in Table 5.

The different nature of the curves of the rate of emulsion saponification as a function of temperature and the high reaction rate when aldehydes are present,

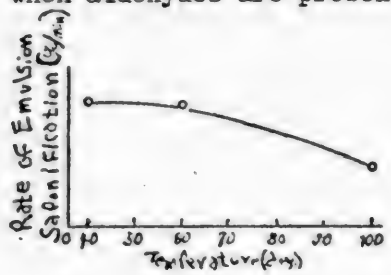

Fig. 3

TABLE 5

Effect of Adding Formaldehyde Upon the Rate of Saponification of Cottonseed Oil

Time, hours	Degree of saponification (per cent) at various quantities of formaldehyde per 100 g of oil			
	0.31 g	0.68 g	1.24 g	2.48 g
0.25	41.0	57.4	57.6	–
0.5	59.0	61.3	63.4	–
1.0	62.3	–	70.0	87.8
2.0	68.5	71.0	73.0	88.8
3.0	72.9	81.0	83.0	89.6
4.0	77.5	91.7	–	91.8
5.0	91.1	–	91.7	97.6

as compared to the alcohols, indicates that the action of the aldehydes not only involves a change in the dispersion, but that they possess still other mechanisms for accelerating the reaction. It is natural to suppose that the aldehydes also serve as alkali carriers.

This is borne out by the resemblance between the curves for the stage of accelerated saponification with aldehydes present and the same curves for phenol and naphthol. This latter circumstance may be explained as due to the singularities of the carbonyl group – its tendency to enter into addition reactions. It may be supposed that in the present case an unstable compound with the alkali is formed.

All the foregoing justifies our speaking of aldehydes and particularly of acetaldehyde, as exceptionally valuable catalysts in the cold saponification of fats and oils.

The catalytic action of acetaldehyde in this instance doubtless exceeds that of ethyl alcohol.

The catalytic ability of acetaldehyde involves a sharp decrease in the surface tension at the oil – concentrated alkali solution boundary. According to our experimental data, it is 0.1 dyne/cm under optimum conditions.

The dispersion of the emulsion is very high in the presence of acetaldehyde.

SUMMARY

1. A study has been made of the "catalytic" action of alcohols on the rate of saponification.

2. It has been shown that adding ethyl, butyl, and isoamyl alcohols sharply raises the velocity of this process in the emulsion stage of saponification.

3. The "catalytic" action of alcohols increases as their surface activity at the oil – concentrated alkali solution interphase boundary rises and is related to an increase in the system's dispersion.

4. A study has been made of the catalytic action of formaldehyde and acetaldehyde upon the rate of saponification of cottonseed oil by concentrated alkalies.

5. It has been shown that the aldehydes, and especially acetaldehyde, are splendid catalysts of the "cold" saponification process.

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Received December 3, 1947.

THE MECHANISM OF THE FRIEDEL-CRAFTS REACTION

X. THE MECHANISM OF THE CATALYTIC ACTION OF ALUMINUM CHLORIDE [1]

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Many theories have been advanced to explain the catalytic action of aluminum chloride in the Friedel-Crafts reaction, as well as in other conversions in which it serves as a catalyst, most of them being based upon the formation of coordination compounds of the catalyst with one reaction component or another. Coordination compounds of aluminum chloride with hydrocarbons [2], with alkyl halides [3], and with hydrogen chloride [4] have been cited in this connection, and even ternary complex groups of all reacting substances [5], various authors attributing different structures to them. The supposition has also been voiced that all the coordination compounds mentioned, or, at any rate, most of them, are harmful compounds that deactivate the catalyst [6].

It should be noted that the weak point in all these theories is their completely ignoring the well-known fact that aluminum chloride has a double molecular weight, corresponding to the formula Al_2Cl_6.

In view of the fact that the coordination compounds of aluminum chloride are of basic importance in explaining its catalytic activity, our attention was first attracted to these substances.

We studied the properties and structure of the coordination compounds of aluminum chloride, and found that it reacts with aromatic hydrocarbons to form compounds of the following composition [7]: $Al_2Cl_6 - 6ArH \cdot HCl$, and with alkyl halides to form compounds with the formula [8]:

$$[AlCl_2 \cdot nRCl]^+[AlCl_4]^-,$$

where the coefficient n is a variable depending on the concentration of the solution, the nature of the solvent, etc.

During these investigations we reached the conclusion that the decisive factor in the catalytic action of aluminum chloride is the formation of bipolar compounds, like the formula described above for co-ordination compounds of aluminum chloride with alkyl halides. As for the role of these coordination compounds during the course of the reaction, it boils down to their purely catalytic action, owing to the fact that each of the oppositely charged parts of such a bipolar molecule can then activize one of the reaction components. From this standpoint, it is of the greatest importance to elucidate the catalytic activity of the free molecule of aluminum chloride, which is combined into any coordination compound. Böeseken [6] endeavored to do this for the monomeric form of aluminum chloride, attributing to it the action of the existence of a strong positive pole near the aluminum atom. We know, however, that aluminum chloride has a double molecular weight and that in the dimer form it does not have a dipole moment [9]. Obviously, this fact cannot be ignored in considering its catalytic activity.

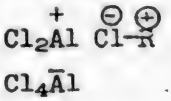
An explanation of this problem must be sought for in the structure of the dimeric molecule of aluminum chloride.

Earlier, we demonstrated [8] that the structure of the aluminum chloride molecule might be represented by the following diagram

which determines the high reactivity of this substance, not explainable by means of Werner's classical formula.

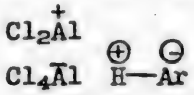
It may be stated that it is this very structure of aluminum chloride that is responsible for the activation of molecules of organic compounds and, thus, for its unusual catalytic activity.

Thus, the action of aluminum chloride in this reactive form upon a molecule of an alkyl halide may be represented as follows:

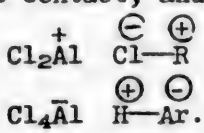


This results in the polarization of the C–Cl bond and the activation of the chlorine atom.

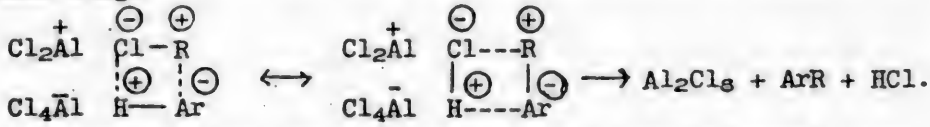
When aluminum chloride acts upon a molecule of an aromatic hydrocarbon, the C–H bond is weakened, and is also polarized:



When a coordination compound of aluminum chloride and a halogen derivative encounters a molecule of an aromatic hydrocarbon, the molecules of all three components come into close contact, and the following activation state results:

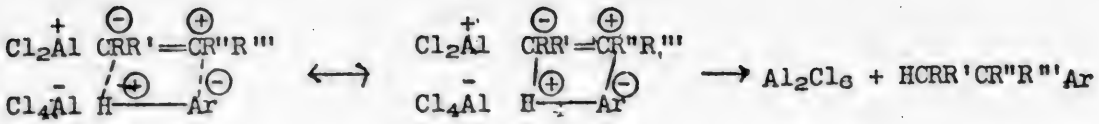


Because the electrons are not localized at any specific point in this case, the electron cloud interaction takes place not only between the atoms of chlorine and alkyl carbon or between the hydrogen and the aryl carbon, but a new interaction makes its appearance: between the atoms of chlorine and hydrogen, as well as between the alkyl and aryl radicals. All this may be represented by means of the following transitional stage:

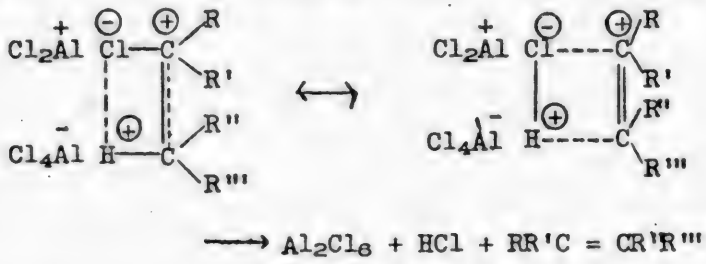


in which the old bonds have not yet been broken, while the new ones are just being established. The next to the last structure illustrated above is responsible for the possibility of the reaction continuing further, splitting off hydrogen chloride and forming an alkylated aromatic compound.

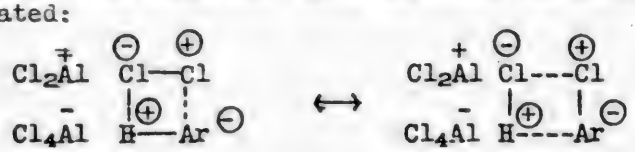
Benzene may be alkylated by olefin halides as well as alkyl halides. The activation of the former by aluminum chloride involves polarization of the double bond, the transitional stage of this reaction, with subsequent production of an alkyl benzene, being as follows:

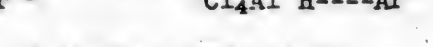


This diagram of the alkylation reaction is of quite general applicability; it may be applied with equal success to all other processes that are catalyzed by aluminum chloride. Thus, the atoms of hydrogen and chlorine may belong to a single molecule: an alkyl halide. The hydrogen chloride will then be split off, forming an olefin:



In a chlorination reaction, both the chlorine molecule and the organic compound are activated:

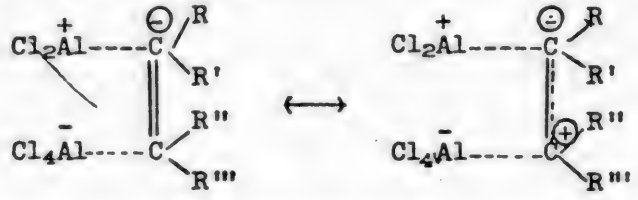




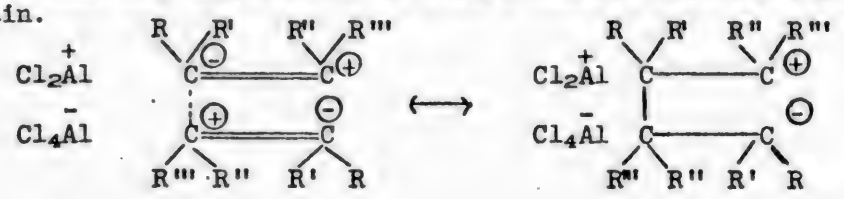
The dehydrogenating effect of aluminum chloride upon hydrocarbons is described similarly. Here two hydrogen atoms, attached to adjacent carbon atoms, are activated.

The direction in which the C – H bonds are polarized depends on the nature of the substituents attached to the carbon atoms. The Scholl reaction and the intermolecular condensation of aromatic rings, with the liberation of hydrogen, are particular examples of this process.

In a polymerization reaction, two variants are possible. In the first, one molecule of the olefin is activated:



the bipolar molecule with an opened double bond that is formed then beginning a chain reaction to form a high polymer. In the other variant, two molecules of the olefin are activated at once and they combine to form a dimeric molecule capable of continuing the chain.



These concepts may be successfully applied to other catalysts that act like aluminum chloride. Most of these substances likewise possess double molecular weight in solutions and vapors. As in aluminum chloride, their structures are similar bipole structures.

These substances include aluminum bromide and iodide, ferric chloride, antimony trichloride, gallium trichloride, indium trichloride, etc. All the notions concerning the mechanism of catalytic action set forth above for aluminum chloride probably hold good for them as well.

Besides these substances, there also are catalytically active halogens such as boron fluoride, which, though not dimeric themselves, can readily constitute active coordination compounds such as $(C_2H_5)_2\overset{+}{O}-\bar{B}F_3$. According to the diagrams developed above, the presence of a dipole is responsible for the catalytic activity of this coordination compound. In this connection, it is of some interest that even boron fluoride cannot catalyze the alkylation of benzene with alkyl halides; only when substances are used with which it forms fairly stable coordination compounds, such as olefins and alcohols, does this reaction become feasible. It is also well known that boron fluoride is activated when ethers and, especially, phosphoric acids are added to it [10], forming bipolar coordination compounds.

These examples suffice to illustrate the fundamental idea proposed by us to elucidate the mechanism of the catalytic action of aluminum chloride and related substances: the activation of two atoms of organic substances because of the presence of a powerful, constant dipole or of a bipolar structure in the catalyst molecule. This does not mean, to be sure, than any dipole molecule or any substance possessing a bipolar structure can act as a catalyst for all these reactions; this requires the maintenance of definite conditions with respect to the strength of the electric field, the distance between centers of opposite charge, etc.

We consider the recognition of the well-known fact of the dimeric nature of aluminum chloride to be the essential merit of the suggested notions concerning the mechanism of its catalytic action. All previous theories have completely ignored this fact, arbitrarily assuming it to be a monomeric compound.

The action of aluminum chloride in all reactions in which it acts as a catalyst is elucidated by us from a single point of view. We have deliberately passed over all complicating circumstances that arise in particular cases, stressing the general factors applying to all of them. This universality of the picture may give rise to some lack of precision in any individual reaction. The essence of the catalytic activity of aluminum chloride always remains the same; it is merely complicated and obscured by other, more or less secondary, processes.

SUMMARY

1. The catalytic activity of aluminum chloride and similar substances is explained as the result of the existence in the catalyst molecule of a powerful, constant dipole or a bipolar structure.

2. This notion is used to set forth new diagrams for the mechanism of the Friedel-Crafts reaction, dehydrogenation, chlorination, polymerization, and others, bearing in mind the dimeric nature of aluminum chloride and the structure of its molecule.

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February 20, 1948.

THE SYNTHESIS OF γ-ACETYLENE GLYCOLS BY THE GRIGNARD-IOTSICH AND FAVORSKY-BABAYAN REACTIONS

A. D. Petrov and E. V. Mitrofanova

The synthesis of saturated and unsaturated alcohols and glycols of differing structure by the Grignard reaction, which was extensively employed by Z. Iotsich to produce acetylene glycols, has been the subject of numerous research papers [1]. As a result of these researches, we are fairly well acquainted with the general nature of the mechanism of the reaction, as well as with its special peculiarities, due to the structure of the various oxo compounds or Mg-alkyl halides. We know, for example, that aliphatic ketones of the $C_nH_{2n+1}-CO-C_nH_{2n+1}$ type react with alkylmagnesium halides containing active saturated, as well as unsaturated, radicals to form tertiary alcohols. But ketones with side chains in the alpha position to the carbonyl group, such as, say, di-isopropyl ketone, with saturated branched alkyl halides (of the $BrMgC\begin{smallmatrix}C\\C\end{smallmatrix}$ type), do not form tertiary alcohols, but are reduced owing to steric hindrances or their low reaction rates. And at the same time di-isopropyl ketone readily reacts with $MgBr-C\equiv C-MgBr$, forming the corresponding acetylene glycol [2] with a high yield. We also know that both the aliphatic unsaturated and the aromatic aldehydes (such as acrolein and benzaldehyde), which tend to react only at the 1,2 position, yield disecondary acetylene glycols. Some ketones with a double bond at the α-β position to the carbonyl group react normally to form tertiary alcohols, not only with active alkyl halides of the $MgBrC\equiv CMgBr$ type, but even with such halides as $MgBrC_2H_5$, and (n-)$MgBrC_8H_{17}$; we have in mind mesityl oxide and its higher analogs, [3]. Only some of the ketones of this type react partially or entirely in a different manner, depending upon the structure of the alkyl halide that reacts with them. According to Kohler [4], ethylmagnesium bromide reacts, say, with benzal methyl ethyl ketone to the extent of 70% at the 1,4 position and with $MgBrC_8H_5$ to the extent of 40%, owing to the addition of the Grignard reagent to the conjugated group of double bonds, in accordance with the Thiele rule:

$$\overset{4}{-}C=\overset{3}{C}-\overset{2}{C}=\overset{1}{O} + RMgX \rightarrow \overset{R}{\overset{|}{C}}-C=C-\overset{MgX}{\overset{|}{O}} \xrightarrow{+H_2O}$$

$$\xrightarrow{+H_2O} -\overset{R}{\overset{|}{C}}-R=C-OH \longrightarrow -\overset{R}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}-C=O,$$

Benzalacetone reacts 60% with $MgBrC_2H_5$ at the 1,4 position, but only 12% with $MgBrC_8H_5$. Benzalacetophenone reacts completely with both of these reagents only in the 1,4 position. But as Gilman [5] has pointed out, even this latter ketone reacts only at the 1,2 position with active organometallic compounds, such as phenylpotassium.

But although we know the rules governing the synthesis of alcohols and glycols, including acetylene glycols (by the Grignard synthesis), very little work has been done on the synthesis of the acetylene glycols by the Favorsky method. A few ketones were used (with positive results and high yields) in the research work done by A.E. Favorsky [6], A.T. Babayan [7], A.D. Petrov [8], A.I. Zakharova [9], and others, viz.: acetone, diethyl ketone, methyl hexyl ketone, and cyclohexanone and its homologs

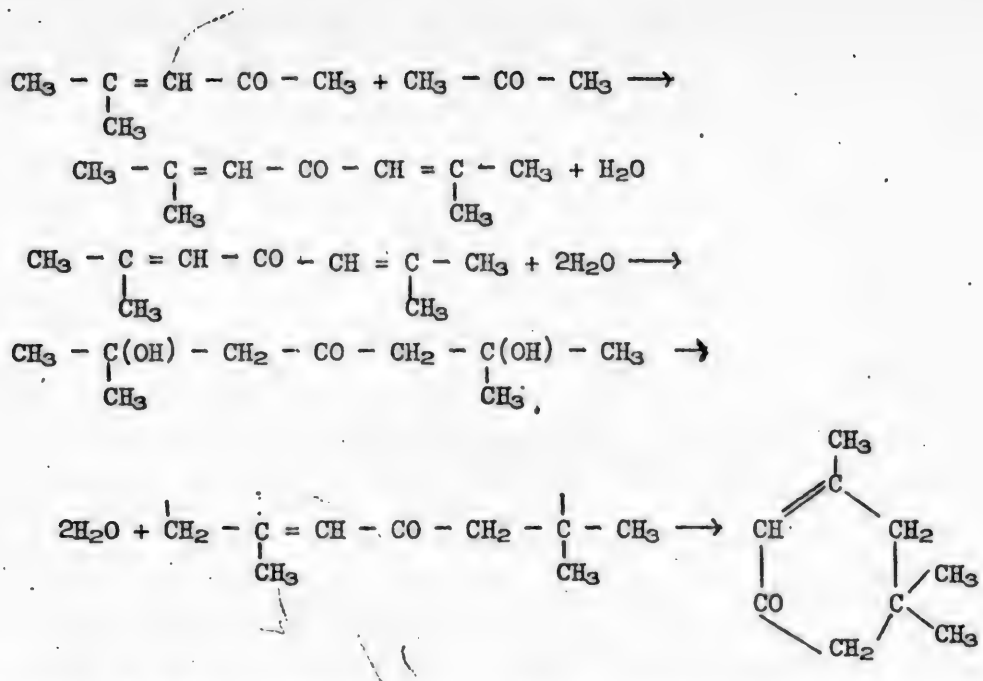
acetophenone and benzophenone. There still is not much available data on the influence of the structure of one ketone or another upon the course of the synthesis. Nonetheless, in this reaction, which resembles the Grignard synthesis so much, we doubtless are dealing with the addition of acetylene or, as some believe, of potassium acetylide at the carbon-oxygen multiple bond (C=O). Furthermore, I.N.Nazarov [10], noticing that hexamethylacetone readily reacts with vinylacetylmagnesium bromide to form a tertiary alcohol (whereas Carothers [11] was unable to synthesize this alcohol with a yield higher than 1% by condensing hexamethylacetone with vinylacetylene in the presence of $NaNH_2$), expressed the supposition that only the Grignard synthesis affects the C=O bond, while the Favorsky reaction involves adding the enol form of the ketone at the carbon-carbon bond. He also noted the negative result of a condensation with acetaldehyde and mesityl oxide and attributed it to tarring as the result of the alkali's action. A.T.Babayan, however, using benzophenone and successfully effecting this synthesis with a high yield, demonstrated that non-enolizing ketones also enter into the Favorsky reaction, thus casting doubt upon Nazarov's outline. Piganiol [12] succeeded in effecting the synthesis of phenyl-1-propynol-1 from benzaldehyde and acetylene by using deep chilling and potassium hydroxide that had been rendered as anhydrous as possible. Lastly, Seguin [13] recently observed that it was even possible to synthesize the acetylenic alcohols of such aldehydes as acetaldehyde and butyraldehyde at a temperature of less than -5° in the presence of KOH + $NaNH_2$.

In the present research we were able, for the first time, to synthesize the acetylene glycols of the following ketones: n-diamyl ketone, di-isopropyl ketone, n-dipropyl ketone, and n-didecyl ketone under the standard conditions of the Favorsky-Babayan reaction, in an ether medium and at a temperature of +15°. The table gives the yields of the corresponding α-acetylene glycols, which testify to the fact that the so-called steric hindrances play a larger part in this reaction than they do in the Grignard reaction, possibly because of the lower reaction rates of the components.* It may be supposed that either the reaction does not involve the intermediate formation of potassium acetylide or that the concentration of the latter is too low and it is less active than $MgBrC{\equiv}CH$. We were altogether unable to synthesize the acetylene glycols of benzaldehyde and benzalacetophenone, even when we complied with the conditions recommended by Piganiol and Seguin. The reason for this was not tarring (the ketones remained unchanged), but the fact the weakly ionized acetylene could not be added at the 1,2 position, i.e., at the carbon oxygen bond; its addition at the 1,4 bond or – in practice – at the 3,4 bond due to isomerization, can be effected only for typical organometallic compounds. It could not occur in this case, of course.

Ketone	Yield of acetylene glycol, %
C–C–C–CO–C–C–C.....	60
C–C–CO–C–C ..... (C, C)	26
$n\text{-}C_5\text{–CO–}C_5$	35
$n\text{-}C_{10}\text{–CO–}C_{10}$.....	12

The results we obtained with mesityl oxide were interesting. Instead of the glycol corresponding to this ketone (synthesized by Iotsich in a Grignard reaction), we recovered a small amount of a crystalline product, which proved to be the acetylene glycol corresponding to isophorone. Furthermore, we were unable to synthesize the acetylene glycol from a separate batch of isophorone. An experiment on the condensation of acetone performed by one of the present authors [14], in which mesityl oxide, isophorone, and xylitone were recovered, with isophorone being again obtained from the latter by hydration, leads us to believe that the formation of isophorone may be explained as follows:

*We were able to eliminate the effect of steric hindrances by changing the synthesis conditions, thus obtaining glycol yields from the di-isopropyl ketone and didecyl ketone that were 60 to 90% of the theoretical (these conditions will be discussed in a subsequent article.)



the formation of the acetylene glycol of isophorone being due to the addition of acetylene to the intermediate saturated form of the aliphatic keto glycol (A). Another possible explanation for the formation of the glycol in this case is the isomerization of 1,1,3-trimethylcyclohexen-3-one-5, at the instant it is formed, to 1,1,3-trimethylcyclohexen-2-one-5. Thus, unlike the Grignard reaction, not only cannot ketones of the mesityl oxide type enter into the Favorsky reaction (the applicability of which is more limited), but neither can mesityl oxide itself, since highly enolized ketones of this type apparently tend to react only at the 1,4 position, i.e., like the reaction of benzalacetophenone with the Grignard reagent (which does not take place, however, owing to the weak ionization of acetylene).

EXPERIMENTAL

Tetraisopropylbutynediol. 35 liters of acetylene were passed through a reaction mixture of 80 g of potassium hydroxide, 25 g of di-isopropyl ketone, and 200 ml of ether at 10-15° for four hours with vigorous stirring. Then another batch of the ketone was added (25 g and 100 ml of ether), and stirring was continued for another hour. After standing for 15 hours, the mixture was decomposed with water, 14.5 g (26% of the theoretical) of a crystalline product with a m.p. of 107° being recovered from the ether layer. Iotsich [15] gives the m.p. of this glycol, synthesized by him from acetylenedimagnesium dibromide, as 106-107°.

11.70 mg substance: 32.45 mg CO_2; 12.49 mg H_2O.
13.61 mg substance: 37.75 mg CO_2; 14.49 mg H_2O.
Found %: C 75.7, 75.69; H 11.94, 11.91.
$C_{16}H_{30}O_2$. Calculated %: C 75.56; H 11.97.
Found: M 260.40.
$C_{16}H_{30}O_2$. Calculated: M 254.24.

0.0542 g substance: 9.8 ml CH_4 (0°, 760 mm)
Found %: OH 13.81.
$C_{16}H_{28}(OH)_2$. Calculated %: OH 13.37.

The liquid fraction, 30 g of which was recovered, had a b.p. of 150-160° and, according to preliminary analysis (determination of the elementary composition

and the number of hydroxyl groups), apparently was a mixture of an acetylene alcohol and the product of its dehydration.

Tetrapropylbutynediol. 30 g of KOH and 60 g of dipropyl ketone with a b.p. of 141-144°, and 250 ml of ether were used. This yielded 40 g of a glycol with a m.p. of 119° (this is the same melting point as given by Dupont, who synthesized this glycol by a Grignard reaction [16]. The liquid fraction totaled 6 g (10%) with a b.p. of 77-83° at 15 mm. The glycol was analyzed.

Found: M 263.1.
$C_{16}H_{30}O_2$. Calculated: M 254.24

0.0205 g substance: 3.7 ml CH_4 (0°, 760 mm).
Found %: OH 13.78.
$C_{16}H_{28}(OH)_2$. Calculated %: OH 13.37.

Tetra-amylbutynediol. 15 g of di-n-amyl ketone with a m.p. of 14.5°, 12 g of KOH, and 175 ml of ether were used. The reaction conditions were the same as previously. 5.7 g (38%) of a glycol with a m.p. of 126° was isolated (apparently synthesized for the first time).

5.830 mg substance: 10.394 mg CO_2; 6.620 mg H_2O.
5.045 mg substance: 14.509 mg CO_2; 5.730 mg H_2O.
Found %: C 78.50, 78.57; H 12.70, 12.72.
$C_{24}H_{46}O_2$. Calculated %: C 78.6; H 12.6.

0.0395 g substance: 4.7 ml CH_4 (0°, 760 mm).
Found %: OH 9.09.
$C_{24}H_{46}O_2$. Calculated %: OH 9.28.

0.0488 g substance: 18.43 g benzene: Δ t 0.035°.
Found: M 378.0.
$C_{24}H_{46}O_2$. Calculated: M 366.4.

Tetradecylbutynediol. Didecyl ketone was synthesized from hendecanoic acid and had a m.p. of 63° (Picard and Kenyon [17] give the m.p. as 64°). 10 g of the ketone, 12 g of KOH, and 400 ml of ether were used. The ketone did not dissolve all at once, but as the acetylene was passed through. 1.5 g of the glycol, with a m.p. of 118°, was synthesized. 8.5 g of the unreacted ketone was recovered.

0.1148 g substance: 0.3431 g CO_2; 0.1389 g H_2O.
Found %: C 81.51; H 13.44.
$C_{44}H_{86}O_2$. Calculated %: C 81.65; H 13.40.
Found: M 648.4.
$C_{44}H_{86}O_2$. Calculated: M 649.69.
0.0758 g substance: 51 ml CH_4 (0°, 760 mm).
Found %: OH 514.
$C_{44}H_{84}(OH)_2$. Calculated %: OH 5.27.

Synthesis of the glycol $C_{20}H_{30}O_2$ from mesityl oxide. The glycol was synthesized in a Favorsky reaction at a temperature of -5 to -10°. As considerable tarring occurred at that temperature, we were unable to separate the synthesized crystalline product from the tarry substances; we therefore repeated the synthesis at a lower temperature. The reaction was carried out in two stages in a sulfuric-ether medium. The first stage – the production of the acetylene alcohol – was carried out at -45 to -50°. The second stage, i.e., the addition of the second half of the quantity of ketone required for the reaction – was carried out at room temperature. The reaction product consisted of a thick, sirupy, cherry-red liquid (72%), and 2% of crystals with a m.p. of 143°; the losses constituted 26%.

Vacuum distillation of the liquid product at 4 mm yielded an initial fraction with a b.p. of 103-107° and n_D^{18} 1.4766. This fraction yielded a semicarbazone with a m.p. of 190°. As we know, the melting point of the semicarbazone of isophorone is 190-191°.

Analysis of the crystals with a m.p. of 143°.

3.300 mg substance: 9.505 mg CO_2; 3.090 mg H_2O.
3.593 mg substance: 10.374 mg CO_2; 3.394 mg H_2O.
Found %: C 78.6, 78.79; H 10.44, 10.57.
$C_{20}H_{30}O_2$. Calculated %: C 79.4; H 10.0.

0.05 g substance: 7.3 ml CH_4 (0°, 760 mm).
Found %: OH 11.16.
$C_{20}H_{28}(OH)_2$. Calculated %: OH 11.25.

0.049 g substance: 15.99 g benzene: Δt 0.050°.
Found: M 306.45.
$C_{20}H_{30}O_2$. Calculated: M 302.

An endeavor to synthesize the glycol from isophorone (m.p. 112° at 11 mm, n_D^{20} 1.4768, d_4^{20} 0.926) at -50° or under the Favorsky-Babayan conditions at +15° did not yield a crystalline product.

SUMMARY

1. The acetylene glycols of n-dipropyl ketone, di-isopropyl ketone, n-diamyl ketone, n-didecyl ketone, and mesityl oxide, have been synthesized for the first time by the Favorsky reaction. It has been established that the yields of the acetylene glycols of di-isopropyl ketone and didecyl ketone are considerably lower than is the case for the other ketones listed. Mesityl glycol yields a glycol that does not correspond to this ketone, but to isophorone.

2. Several parallels and comparison were made between syntheses of acetylene glycols by the Grignard and the Favorsky reactions. Arguments and proofs are submitted in favor of the addition of the Grignard reagents as well as the free acetylene to the carbon-oxygen multiple bond during the synthesis of the glycols.

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Received May 5, 1948.

THE DISLODGEMENT OF SUBSTITUENTS IN THE AZO COUPLING OF PARA-SUBSTITUTED DIMETHYLANILINE

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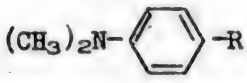
The literature contains numerous references to the dislodgment of existing substituents in nitration, nitrosation, and halogenation. When 4-dimethylaminobenzaldehyde is brominated, for example, we get 4-bromodimethylaniline, and when it is nitrosated, we get 4-nitrosodimethylaniline [1].

The dislodgment of substituents is also observed fairly frequently in azo coupling. This phenomenon was first described by Nietzki and Guiterman in 2-hydroxy-1-naphthoic acid [2]; later, Kostanecki and Zibell [3] found that the carboxyl group is dislodged (CO_2 is evolved) during the azo coupling of 4-hydroxybenzoic acid. It has also been found that an aldehyde group is dislodged (apparently as formic acid) when a diazonium salt acts upon 4 dimethylaminobenzaldehyde [4]. S.F.Filippychev and M.A. Chekalin [5] have described the dislodgment of an aryl azo group during a reaction with a more active diazonium salt.

Notwithstanding the large amount of data available by now, we still have no theory of this phenomenon at all, nor do we know what properties a radical R must have for it to be dislodged during azo coupling, say, of para derivatives of dimethylaniline:

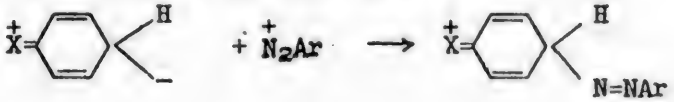


(I)

The present paper comprises an endeavor to provide an explanation; for the reasons set forth below, it seems to me that the ability to split off the R radical is bound up with the probability of the existence (or stability) of the R^+ cation.

According to contemporary notions, azo coupling, like all other substitution reactions, takes place only with compounds exhibiting resonance and producing a negative charge on a carbon atom:

We may assume that the first act of this reaction is the addition of the diazonium cation to the negatively charged carbon atom [6,7]:



(II)

But for the intermediate product (II), which has a quasi-quinoid structure, to be converted into the azo end product, a proton must be detached. Thermodynamic

considerations make it seem unlikely, in general, that the proton is detached directly as such; apparently, the proton is always detached as a compound with a base, i.e., when the intermediate compound (II) encounters molecules of water or other molecules and ions acting as bases.

There are many reasons for thinking that in the general case an acid-basic catalysis takes place during substitution reactions [8] and, in our particular example, during azo couplings. When azo coupling is effected in an aqueous medium, water molecules, acetate ions, pyridine, or hydroxyl ions may act as the base (B) that combines with the proton:

If some radical R is situated at the para position to the activating group instead of a hydrogen atom, we get azo coupling, as stated above, with detachment of the R radical; in other cases (with a different R) no azo coupling occurs, or the azo grouping is in the ortho position to X. Apparently, there is no reason to suppose that azo coupling occurs in some other manner when a radical is dislodged: as in the case of an unsubstituted compound, the intermediate product (III):

(III)

may be converted into a true azo compound only when the R radical is detached as an R^+ cation. We cannot state definitely whether acid-basic catalysis, i.e., the capture of a cation by a base, is present here as well; we can only suppose that if such catalysis takes place, it plays a much less important part in the dislodgment of a fairly complex radical. For hydrogen occupies a very special position in this respect, owing to the tendency toward the formation of hydrogen bonds. In any event, the detaching of the R radical as an R^+ cation or its combination with a base, RB^+, is all the more likely in that the cation is evidently more stable than the proton or the hydroxonium ion. Hence what we need to solve the problem of the detaching of the R radical is data on the equilibrium of the following reactions:

$$R^+ + 2H_2O \rightleftharpoons ROH + OH_3^+.$$

The higher the constant of this reaction (the smaller pK):

$$K = \frac{[ROH][OH_3]}{[R^+]}; \qquad pK = pH + \log \frac{[R^+]}{[ROH]},$$

the less able is the R^+ cation to exist, and vice versa. Unfortunately, we have very little experimental data on equilibria of this sort, and hence we cannot make any use of them. But the degree of stability of the R^+ cation as compared to that of the proton may be evaluated approximately from the heats of hypothetical reactions (Q_1, Q_2, Q_3):

$$RH(g) + H^+(g) = R^+(g) + H_2(g) + Q_1;$$
$$RCH_3(g) + H^+(g) = R^+(g) + CH_4(g) + Q_2;$$
$$RC_6H_5(g) + H^+(g) = R^+(g) + C_6H_6(g) + Q_3.$$

The heats of these hypothetical reactions may be calculated if the heats of formation are known for the elements (Q_0) of the cations R^+, H^+, methane, benzene and of the substituted RH, RCH_3, and RC_6H_5:

$$Q_1 = Q_0(R^+g) - Q_0(H^+g) - Q_0(RHg);$$
$$Q_2 = Q_0(R^+g) + Q_0(CH_4g) - Q_0(H^+g) - Q_0(RCH_3g);$$
$$Q_3 = Q_0(R^+g) + Q_0(C_6H_6g) - Q_0(H^+g) - Q_0(RC_6H_5g).$$

If we take the stability of the R^+ cation as compared to the stability of the hydroxonium ion, we have to use the heats of reaction Q_1', Q_2', and Q_3' instead of the heats of reaction Q_1 Q_2, and Q_3.

$$RH(g) + H_3O^+(g) = R^+(g) + H_2(g) + H_2O(g) + Q_1';$$
$$RCH_3(g) + H_3O^+(g) = R^+(g) + H_2O(g) + CH_4(g) + Q_2';$$
$$RC_6H_5(g) + H_3O^+(g) = R^+(g) + C_6H_6(g) + H_2O(g) + Q_3'.$$

It may be readily shown that the difference between Q_1' and Q_1, like that between Q_2' and Q_2, is the proton affinity of water (P_{H_2O}):

$$Q_1 - Q_1' = Q_2 - Q_2' = Q_3 - Q_3' = P_{H_2O} \sim 184 \text{ Cal.}[9].$$

Table 1 gives the heats of formation of various compounds at constant pressure in large calories; some of them were taken directly from Bichowsky's and Rossini's handbook [10]; others were computed from the heats of combustion (applying Swentoslawski's corrections); the heats of formation of CO_2 and H_2O were taken as 94.45 and 68.37 Cal, respectively [10].

TABLE 1

Heat of Formation of R^+, RH, RCH_3, and RC_6H_5

R	$Q_o(R^+g)$	$Q_o(RH\ g)$	$Q_o(RCH_3\ g)$	$Q_o(RC_6H_5)$
H	-365.58[10]	0	+18.24 [10]	-11.6 L [17]
F	-462.95 [10]	+64.0 [10]		+31.8 L [27]
Cl	-329.46 [10]	+22.06 [10]	+20.1 [10]	+7.04 L [14]
Br	-298.92 [10]	+8.65 [10]	+8.5 [10]	-9.8 L [14]
I	-267.54 [10]	-8.89 [10]	-4.5 [10]	-24.7 L [15]
NO_2	-291.6 [11]	–	+18.6 [10]	-1.3 L [16]
CN	-420.3 [12]	-30.7 [10]	+19.4 [10]	-30.8 L [23]
CH_3	-288.8 [12]	+18.24 [10]	+20.96 [10]	-2.5 L [24]
C_2H_5	-275.2 [18,19]	+20.96 [10]	+26.3 [27]	+5.6 L [25]
C_2H_3	-339 [18,20]	-11.0 [10]	-6.4 [21]	-25.4 L [22]
NO	-241.6 [13]	–	–	-4.6 S [28]
HCO	-149 [28]	+28.7 [10]	+44.0 [10]	+21.7 L [34]
HOCO	-242 [28]	+88.65 [10]		+940 S [29]
HO	-298 [31]	+ 57.8 [10]	+48.44 [10]	+38.8 S [32]
CO_2^-	+94.45 [10]	+107 [30]		
O^-	-59.1 [10]	+40.4 [30]		

I computed the heats of formation of the CH_3^+, NO_2^+, CN^+, NO^+, HCO^+, $COOH^+$, and HO^+ ions from experimental data on the heats (potentials) of ionization from the works referred to in Table 1: the accuracy of these data was not very high; 5 Cal may be taken as the minimum value of the error involved. The value for $Q_o(CN^+)$ seems to be somewhat low; it is possible that the ionization potential is given for the formation of CN^+ in the excited state. The heats of formation of the various phenyl compounds are known only for the condensed state; inasmuch as the problem under discussion requires comparative values, the heats of formation of RC_6H_5 in the condensed state were simply taken for the computation of Q_3.

I computed the heats of formation of the $C_2H_5^+$ and $C_2H_3^+$ ions from the heats of dissociation (the binding energies) of the respective iodine derivatives into iodine and the radicals according to the figures given by Butler and Polyani [18], and by combining the heats of formation of these radicals with the ionization heats of these radicals, namely, for ethyl, from the data of Hipple and Stevenson [19], and for vinyl, from the paper by Stevenson [20]. The heat of formation of vinyl

iodide was taken as equal to the heat of formation of ethyl iodide minus the heat of hydrogenation of ethylene (32 Cal). The heats of formation of the gaseous anions $HCOO^-$ and OH^- were computed from the figures given for proton affinity in K.B.Yatsimirsky's paper [30].

The symbols L and S denote that the heats of formation were calculated for the liquid or solid state. This yields the following values for Q_1, Q_2, and Q_3

TABLE 2

Values of the Heats of Reaction Q_1, Q_2, and Q_3

R	Q_1	Q_2	Q_3	R	Q_1	Q_2	Q_3
H	0	0	0	C_2H_5	+69.4	+82.3	+73.1
F	-161.27	–	-140.8	C_2H_3	+38.6	+51	+40
Cl	+14.0	+34.26	+17.5	NO	–	–	+117
Br	+58.16	+76.4	+64.9	HCO	+188	+191	+183
I	+102.5	+120.8	+111.2	HO	+10	+19	+29
NO_2	–	+73.6	+53.7	CO_2^-	+360	–	–
CN	-22.0	-17.1	-35.5	O^-	+366	–	–
CH_3	+60	+76.0	+70	HOCO	+33.0	–	+18

The values of Q_1 indicate that fluorine ought to be easiest to detach, followed by CN and the others in the following order:

$F < CN < H < OH < Cl < CO_2H < C_2H_3 < Br < CH_3 < C_2H_5 < I < CHO < CO_2^- < O^-$. The values of Q_2 yield the following sequence: $CN < H < OH < Cl < C_2H_3 < NO_2 < CH_3 < Br < C_2H_5 < I < CHO$. The values of Q_3 yield the following sequence: $F < CN < Cl < H < CO_2H < OH < C_2H_3 < NO_2 < Br < CH_3 < C_2H_5 < I < NO < CHO$.

To check the ease with which the radicals can be detached I prepared and tested for azo coupling various para-substitution derivatives of dimethylaniline, which, as we know, does not undergo ortho coupling with the dimethylamino group; if azo coupling takes place, it occurs only with detachment of the para substituent. It was found (cf the experimental section below) that 4-cyanodimethylaniline, 4-chlorodimethylaniline, 4-nitrodimethylaniline, 4-nitrosodimethylaniline, and 4-methyldimethylaniline exhibit no coupling with 2,4-dinitrophenyldiazonium and 4-nitrophenyldiazonium. The following do exhibit coupling with the diazonium salts: dimethylaniline, 4-bromodimethylaniline, 4-iododimethylaniline, 4-dimethylamino benzaldehyde, and 4-dimethylaminobenzoic acid. 4-Hydroxydimethylaniline does not couple with diazonium salts: the diazonium salt is broken down (reduced); this is due to the former's low reduction potential.

In the Q_1, Q_2, Q_3 series, hydrogen ought to be harder to detach than chlorine; but actually this is not the case. Dimethylaniline couples with diazonium salts, whereas 4-chlorodimethylaniline does not. This may be considered confirmation of the hypothesis that hydrogen is not detached as a proton, but as a hydrated oxonium ion. If we compute the respective values of Q_1', Q_2', and Q_3' (the stability of R^+ compared to that of the hydroxonium ion), we find that of the radicals listed above, the formyl radical (the aldehyde group), the CO_2^- ion radical, and the O^- ion radical are detached more easily than hydrogen. The position of the vinyl radical is peculiar; according to the Q_1, Q_2, and Q_3 heats it ought to be harder to detach than the nitro group or bromine. This sequence of readiness of detachment has the following exceptions, however: according to the values of Q_1 and Q_3, methyl ought to be easier to detach than bromine, whereas according to the value of Q_2, it is harder to detach; in reality, methyl is not detached, whereas bromine is. To be sure, the differences in the values of Q_1, Q_2, and Q_3 lie within the range of experimental error. Similarly, NO ought to be easier to detach than

bromine, according to these figures; the contrary is true, in reality: nitrosodimethylaniline exhibits no azo coupling. Apparently, this is due to the well-known resonance of nitrosodimethylaniline:

It must be assumed that resonance strengthens the bond between the NO and the aromatic ring, preventing the detaching of the NO as a cation. 4-Dimethylaminobenzoic acid hardly couples as such; it is more likely that its anion is coupled (CO_2^- detached as CO_2).

These calculations have been performed for a few radicals. In the experimental section we also cite data for the dislodgment of radicals for which no such computations could be made (Table 2). I assume that these figures enable us to reach some qualitative conclusions concerning the nature of the radicals. The circumstance that radicals whose positive ions may exist in resonant forms are readily detached is worthy of note; in these, the positive charge is shifted to the strongly basic amino group, which, therefore, increases the probability of the existence of a

TABLE 3

Azo Coupling of Derivatives of Dimethylaniline $(CH_3)_2NC_6H_4R$

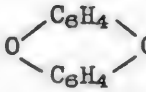
Name	R	Q_3	2,4-Dinitrophenyldiazonium	4-Nitrophenyldiazonium
4-Cyanodimethylaniline.....	CN	-35.5	–	–
Dimethylaniline.....	H	0	+	+
4-Hydroxydimethylaniline...	OH	+29	Diazonium salt breaks down	
4-Chlorodimethylaniline ...	Cl	-17.5	–	–
4-Dimethylaminobenzoic Acid	CO_2H	+18	+	+
4-Bromodimethylaniline.....	Br	+64.9	+	+
4-Methyldimethylaniline	CH_3	+70	–	–
4-Iododimethylaniline.....	I	+111.2	+	+
4-Nitrodimethylaniline.....	NO_2	+53.7	–	–
4-Nitrosodimethylaniline...	NO	+117	–	–
4-Dimethylaminobenzaldehyde	CHO	+183	+	+

cation. Thus, 4,4'-bis-dimethylaminodiphenylmethane, 4,4'-bis-dimethylaminotriphenylmethane, and some of their derivatives exhibit coupling. This apparently is due to the existence of the resonance of the detachable ion referred to:

Thus, the experimental data qualitatively corroborate the sequence of ease of detachment, and it may be considered as proven that the ability of the R radical to be detached is linked to the stability of the R^+ cation. The few departures from this series can be explained rationally, at least qualitatively. It must not be thought that radicals that are not detached in the azo coupling of the para derivatives of dimethylaniline will not be detached from other substitution products; certain data indicate that the contrary is true: the detachability boundary shifts with the nature of the aryl group.

TABLE 4

Azo Coupling of Para Substitution Derivatives of Dimethylaniline for which Q_1, Q_2, and Q_3 Could Not be Computed

Name	R	2,4-Dinitro phenyldiazonium	4-nitrophenyl-diazonium
4-Dimethylaminobenzoic acid...	$-CH_2OH$	+	+
4-Dimethylaminobenzamide.....	$-CONH_2$	+	+
4-Dimethylaminobenzanilide...:	$-CONHC_6H_5$		Slight azo coupling
4-Dimethylaminoacetanilide....	$-NHCOCH_3$	−	−
4-Dimethylaniline-4-sulfo acid	SO_3^-	+	+
4,4'-Bis-dimethylaminodi-phenylmethane.....	$(CH_3)_2NC_6H_4CH_2-$	+	+
4,4'-Bis-dimethylaminobenzo-phenone.....	$(CH_3)_2NC_6H_4CO-$	+	+
4,4'-Bis-dimethylaminotri-phenylmethane.....	$(CH_3)_2NC_6H_4CH(C_6H_5)$	+	+
4,4'-Bis-dimethylaminotri-phenylcarbinol.....	$(CH_3)_2NC_6H_4C(OH)C_6H_5$	+	+
β-(4'-Dimethylaminophenyl)- α-phenylacrylonitrile.....	$C_6H_5C(CN)=CH-$	−	−
2-Nitro-4,4'-bis-dimethylamino-diphenylmethane	$(CH_3)_2NC_6H_3(NO_2)CH_2-$	+	−
2"-Nitro-4,4'-bis-dimethyl-aminotriphenylmethane.....	$(CH_3)_2NC_6H_4CHC_6H_4NO_2$	+	+
3"-Nitro-4,4'-bis-dimethyl-aminotriphenylmethane.....		+	+
4"-Nitro-4,4'-bis-dimethyl-aminotriphenylmethane.....		+	+
9-(Dimethylaminophenyl)-xanthene.....		+	+
4-Dimethylaminobenzaldoxime...	$HON=CH-$	−	−
4-Dimethylaminobenzaldazine...	$(CH_3)_2NC_6H_4CH=N-N=CH-$	−	−

EXPERIMENTAL

I synthesized most of the substances employed for the qualitative tests of azo coupling by the methods described in the literature; the purity of the preparations was checked by determining their melting points (for the solids); sometimes control reactions were performed to prove that no impurities were present. The azo coupling test was made with diazonium salts prepared on paper. 4-Nitrophenyldiazonium was prepared as described [33], by applying a benzene solution of 4-nitroaniline (concentration = 1 mg per ml) to dry paper, and then treating the sheet of paper first with gaseous hydrogen chloride (over hydrochloric acid of 1.19 sp gr.) and then with methyl nitrite fumes. The 2,4-dinitrophenyldiazonium was prepared by applying an alcohol-benzene solution of 2,4-dinitrophenylhydrazine (concentration = 1 mg per ml) to paper, and then treating it with bromine fumes; the excess bromine was blown off the paper. The compound to be tested was dissolved in some highly

volatile organic solvent, most often benzene, and then applied to the prepared sheet of paper with the diazonium salts. If the substance was hard to dissolve in benzene, other solvents were used. Five minutes after the substance under test was applied, the sheet was either tinted or not. If it was tinted (which indicated the presence of azo coupling), the tinting was the same as when dimethylaniline was applied; this testified to the absence of azo coupling at the ortho position or in any other way than by detaching a para substituent. The appearance of tinting and, hence the detachment of a substituent, is denoted in Tables 3 and 4 by the plus sign (+); the absence of tinting is denoted by a minus sign (-).

SUMMARY

1. It has been shown that the ability to detach an R radical during the azo coupling of para substitution derivatives of dimethylaniline depends upon the probability of the existence (or stability) of the R^+ cation.

2. The heats of formation of various cations and the heats of several reactions have been computed.

3. Twenty-six para substitution derivatives of dimethylaniline have been tested for azo coupling by means of qualitative tests with 2,4-dinitrophenyldiazonium and 4-nitrophenyldiazonium.

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Received June 2, 1948.

A NEW METHOD OF CONVERTING THE AMIDES OF CARBOXYLIC ACIDS INTO THEIR NITRILES

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As has already been reported in one of our previous reports [1], the formation of a small amount of benzonitrile was observed in the experimental investigation of a reaction of benzoic acid with sulfamide, evidently in accordance with:

$$C_6H_5COOH + NH_2SO_2NH_2 \longrightarrow C_6H_5CONH_2 + NH_2SO_2OH \longrightarrow$$
$$\longrightarrow C_6H_5CN + NH_4OSO_2OH.$$

As we know, when aryl sulfonic acids and their amides react with amides of carboxylic acids, we also get nitriles [2], mixed imides being formed as intermediate products in accordance with:

$$C_6H_5CONH_2 + ArSO_2OH + ArSO_2NH_2 \rightarrow C_6H_5CONHSO_2Ar +$$
$$+ ArSO_2ONH_4 \rightarrow C_6H_5CN.$$

It is quite probable that when sulfamic acid is reacted with amides of carboxylic acids, mixed imides are likewise formed as intermediate products:

$$C_6H_5CONH_2 + HOSO_2NH_2 \rightarrow [C_6H_5CONHSO_2ONH_4] \rightarrow$$
$$\rightarrow C_6H_5CN + HOSO_2ONH_4,$$

but no experimental proof of this assumption has been supplied. The mechanism of the reaction of sulfamic acid with the amides of carboxylic acid is probably similar to the mechanism of the reaction of aryl sulfonic acids with the amides of carboxylic acids, which were discussed in detail in a previous report, [3], and therefore will not be dealt with here.

The reaction of benzamide with sulfamic acid, or – more precisely – with pyridine sulfamate with an excess of pyridine present, takes place slowly and with poor yields at the boiling point of pyridine, in contrast to the reaction of sulfamide with carboxylic acids in the presence of an excess of pyridine [1]. It is quite possible that the poor yields in the foregoing case are due to the low solubility of pyridine sulfamate in pyridine, whereas sulfamide is readily soluble in pyridine.

Only some 5% of the theoretical quantity of benzonitrile is formed in 10 hours of boiling a mixture of benzamide, sulfamic acid, and pyridine. Incomparably better results are obtained by heating a mixture of benzamide and sulfamic acid without any solvent – the yield of crude benzonitrile is 90.6% of the theoretical, with 82% of the theoretical quantity being recovered after double distillation, it is probable that this figure could be improved by a detailed study of the reaction conditions.

The reaction of sulfamic acid with amides of carboxylic acids is apparently a general one, and, in view of the availability, cheapness, and low molecular

weight of sulfamic acid, it is one of the most satisfactory, and perhaps the most satisfactory of the methods for converting amides into nitriles. The reaction is carried out by mixing the amide carefully with the sulfamic acid and heating the mixture for 10-20 minutes to 180-220° over an oil or air bath, with constant stirring. The volatile nitriles are driven off, and the high-boiling reaction mixture, after cooling, is extracted with suitable solvents, preferably after treatment with water, which extracts the ammonium bisulfite.

We thus produced nitriles of the following acids: acetic (55%), caprylic (78.5%), palmitic (80.5%), benzoic (82%), m-nitrobenzoic (94%), p-nitrobenzoic (94%), p-chlorobenzoic (97%), o-chlorobenzoic (91%), and phenylacetic (72.5%) acids. It is worthy of note that the conversion of acetamide to acetonitrile takes place with a yield of 96.5%, based on sulfamic acid, when two molecules of acetamide are used in the reaction for every molecule of sulfamic acid, part of the acetamide being converted into acetic acid.

Carboxylic acids can also be converted into nitriles directly by heating the acids with sulfamide without any solvent, as follows:

$$RCOOH + NH_2SO_2NH_2 \rightarrow RCONH_2 + HOSO_2NH_2 \rightarrow RCN + HOSO_2ONH_4.$$

This will be dealt with in one of our subsequent reports.

EXPERIMENTAL

Reaction of Benzamide with Sulfamic Acid Dissolved in Pyridine

0.1 mol (12.1 g) of benzamide was mixed with 0.12 mol (11.6 g) of finely pulverized sulfamic acid and 50 ml of anhydrous pyridine.

The mixture was heated to boiling with a reflux condenser over an oil bath and kept at the boiling point for 9 hours, after which the pyridine was driven off in vacuum at 60° over a water bath. 25 ml of water and enough 10.0 N sulfuric acid were added to the residue until an acid reaction was obtained with Congo indicator, after which the volatile products were driven off with steam. The distillate was extracted three times with 50 ml of ether each time; the combined ether extracts were desiccated with sodium sulfate, and the ether driven off. This left 1.2 g of an oily liquid with the odor of benzonitrile. Distillation yielded 0.6 g of a 184-188° fraction. The benzonitrile was converted into m-nitrobenzonitrile for identification. This yielded 0.4 g of m-nitrobenzonitrile, with a m.p. of 115-117°; it exhibited no depression when mixed with a known sample of m-nitrobenzonitrile [4].

Reaction of Benzamide with Sulfamic Acid, Without a Solvent

A mixture of 0.1 mol (12.1 g) of benzamide and 0.15 mol (14.55 g) of sulfamic acid was carefully triturated in a mortar, placed in a Würtz flask, and heated over an oil bath. The temperature of the bath was raised to 200° in 20 minutes, during which time all the reaction mixture liquified. With the bath at 203°, the benzonitrile began to pass over. The bath temperature was raised to 230° in 20 minutes, the vapor temperature rising from 185 to 205°. A total of 9.34 g of benzonitrile was distilled over, i.e., 90.6% of the theoretical; double distillation yielded 8.44 g, or 82%, of the theoretical of benzonitrile, boiling at 185-186°. It was identified in the form of m-nitrobenzonitrile, as before.

Reaction of Acetamide with Sulfamic Acid

A. A mixture of 0.3 mol (17.7 g) of acetamide and 0.4 mol (38.8 g) of carefully pulverized sulfamic acid was heated in an Erlenmeyer flask over an oil bath. At 150° the reaction mass foamed slightly, and acetonitrile began to distil over; this was completed in 30 minutes at a bath temperature of 195°.

The crude acetonitrile recovered totaled 7.65 g, or 62% of the theoretical.

Redistillation yielded 6.75 g of acetonitrile, boiling at 80-82°, i.e., 55% of the theoretical quantity, with a m.p. of -47° (thermometer bulb in the liquid; melting point of a mixed test sample was -46° [5].

B. A mixture of 0.2 mol (11.8 g) of acetamide and 0.1 mol (9.7 g) of carefully pulverized sulfamic acid was heated in an Erlenmeyer flask over an oil bath. Distillation set in at 165° and was complete only after 90 minutes had elapsed with the bath temperature at 220°.

A total of 6.9 g was driven over. The product was distilled extremely slowly with a herringbone dephlegmator, yielding 4.75 g of an 80-100° fraction and 1.4 g of a 100-115° fraction. Redistillation of the first fraction with a herringbone dephlegmator yielded 3.95 g of acetonitrile boiling at 80-84°, i.e., 95.5% of the theoretical quantity, based on sulfamic acid, with a m.p. of -51°; the melting point of a mixed test sample was -49° [5]. Redistillation of the second fraction yielded 0.8 g of acetic acid, boiling at 114-116°, m.p. 14-16°; it exhibited no depression when mixed with known acetic acid.

Synthesis of Caprylonitrile

A well-pulverized mixture of 0.02 mol (2.86 g) of caprylamide and 0.04 mol (3.88 g) of sulfamic acid were heated over an air bath with vigorous stirring. The bath temperature was raised to 200° for 10 minutes and to 210° for the next 10 minutes. This caused the reaction mixture to liquefy and darken. After cooling the reaction product was treated with 20 ml of water and then with 4 batches of ether, 25 ml in each. The combined ether extracts were washed with 2 ml of a 1N solution of soda and desiccated with sodium sulfate. After the ether was driven off, we recovered 2.3 g of a brownish oil, which was distilled at atmospheric pressure. This yielded 1.8 g of caprylonitrile, boiling at 195-197°; sp. gr. 0.8198 at 15°. (1.1883 ml of the substance weighed 0.9742 g) [6].

Synthesis of Palmitonitrile

A thoroughly pulverized mixture of 0.01 mol (2.55 g) of palmitamide and 0.02 mol of sulfamic acid was heated over an air bath to 200° for 10 minutes and from 200 to 210° for the next 10 minutes, with vigorous stirring. The mixture turned brown; after cooling it was a crystalline mass impregnated with an oily liquid.

Treatment with 20 ml of water and 100 ml of benzene caused nearly the whole product to enter into solution, except for a small quantity of brown tar, which was filtered out. The benzene solution was evaporated to 25 ml and chilled. This caused a small amount of an amorphous precipitate to settle out; this precipitate was filtered out, and then the benzene was evaporated to dryness, finally in vacuum. The residue was a light yellow oil, totaling 2.2 g. Vacuum distillation of this oil yielded 1.9 g (80.5%) of palmitonitrile, with a b.p. of 186-188° at 10 mm, as a colorless liquid that slowly crystallizes at room temperature; its m.p. is 28-29° (thermometer bulb in the liquid); it exhibits no depression when mixed with known palmitonitrile [7].

Synthesis of m-Nitrobenzonitrile

A mixture of 0.005 mol (0.83 g) of m-nitrobenzamide and 0.00625 mol (0.61 g) of sulfamic acid was carefully triturated in a mortar and then heated, with vigorous stirring, over an air bath. The air bath temperature was raised to 220° in 20 minutes and kept at 220° for another 5 minutes. Heating caused the mixture to turn slightly brown and to liquefy; toward the end of the reaction it was a liquid mass mixed with solid crystals. After cooling, the solidified mixture was pulverized and treated with three 20-ml batches of boiling benzene; the precipitate was filtered out, and the combined benzene extracts were clarified with charcoal, extracted with 1 ml of 1 N sodium hydroxide, and then evaporated to dryness. The residue

totaled 0.7 g, i.e., 94% of the theoretical quantity of crude m-nitrobenzonitrile. Recrystallization from 100 ml of boiling water yielded 0.4 g of fine colorless needles with a m.p. of 115-117°; they exhibited no depression when mixed with known m-nitrobenzonitrile [8].

Evaporation of the mother liquor yielded another 0.2 g of a product with a m.p. of 115-117°. 0.04 g of m-nitrobenzoic acid was recovered from the alkaline extract.

Synthesis of p-Nitrobenzonitrile

The reaction was similar to that for m-nitrobenzonitrile. It yielded 0.7 g, or 94% of the theoretical quantity of p-nitrobenzonitrile; after recrystallization from water, it was in the form of colorless, fine, flat needles, with a m.p. of 146-147°; it exhibited no depression with known p-nitrobenzonitrile.

Synthesis of o-Chlorobenzonitrile

A mixture of 0.01 mol (1.56 g) of o-chlorobenzamide and 0.02 mol (1.94 g) of sulfamic acid was heated over an air bath to 220° for 10 minutes, with stirring. The mixture turned brown and liquefied, a small amount of the substance distilling over. After cooling, the reaction product was treated with 10 ml of water and with three 25-ml batches of ether. The ether extracts were colorless, whereas the aqueous solution was brown, giving an acid Congo reaction, and with some tar as a deposit. The combined ether extracts were extracted with 2 ml of 1 N sodium hydroxide, the ether was driven off and the residue was desiccated in vacuum over sulfuric acid. This yielded 1.25 g, or 91%, of the theoretical quantity, of o-chlorobenzonitrile with a m.p. of 45-46°; the m.p. was 47-48° after sublimation; it exhibited no depression when mixed with a known sample of o-chlorobenzonitrile [10].

Synthesis of p-Chlorobenzonitrile.

The reaction was like that for the o-chlorobenzonitrile. It yielded 1.3 g of p-chlorobenzonitrile; the product consisted of long, colorless needles with a m.p. of 92-93° after sublimation; it exhibited no depression with known p-chlorobenzonitrile [11].

Synthesis of Phenylacetonitrile

A mixture of 0.02 mol (2.7 g) of phenylacetamide and 0.04 g (3.88 g) of sulfamic acid was heated, with vigorous stirring, over an air bath to 200° for 15 minutes and to 215° for 5 minutes. After cooling, the reaction mixture was treated with 20 ml of water and with two 50-ml batches of ether. The combined ether extracts were washed with 2 ml of 1 N sodium hydroxide, and the ether was driven off (under vacuum toward the end). The residue consisted of 2.0 g of a brown liquid with the odor of benzyl cyanide. Redistillation in vacuum yielded 1.7 g of phenylacetonitrile as a colorless liquid, which boiled at 105-106° and 10 mm. For identification, 0.1 g of the substances was placed in 1.0 g of nitric acid (1.5 sp. gr.) at 0°, and 15 minutes later the mixture was poured over ice. The resulting precipitate was drawn off and recrystallized from alcohol, m.p. 114-115°; it exhibited no depression when mixed with known nitrobenzyl cyanide [12].

SUMMARY

A new method has been developed for converting the amides of carboxylic acids into their nitriles by the action of sulfamic acid. The method has been tried out on several aliphatic and aromatic acids.

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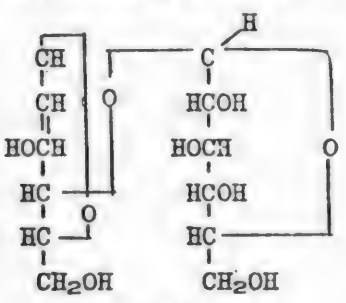
Received June 4, 1948.

DETERMINATION OF THE STRUCTURE OF THE DISACCHARIDES

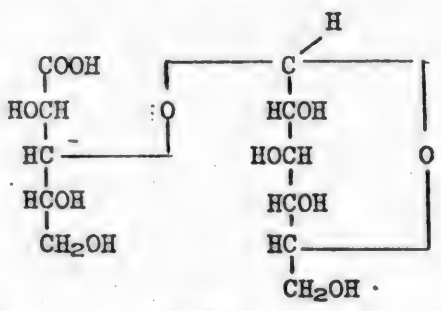
IV. DETERMINATION OF THE STRUCTURE OF CELLOBIOSE [1]

A. M. Gakhokidze

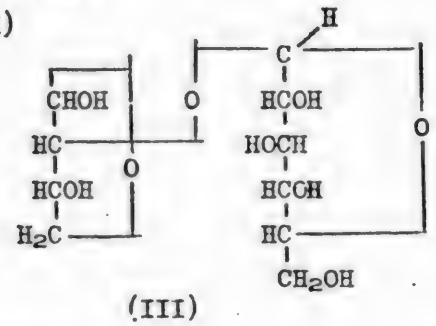
Cellobiose has been converted into cellobial (I) via the octa-acetate and then via acetobromocellobiose and hexa-acetylcellobial [2]. When cellobial was oxidized with potassium permanganate in the presence of potash, glucosido-3-arabonic acid (II) was recovered. Oxidation of the calcium salt of glucosido-3-arabonic acid yielded erythrose glucoside (III).



(I)



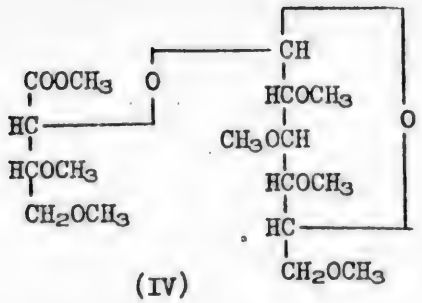
(II)



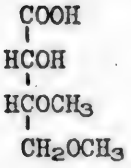
(III)

Erythrose glucoside reduces Fehling's solution and forms a silver mirror, but it does not form an osazone. The latter circumstance indicates the absence of a hydroxyl group at the second carbon atom of the erythrose, and hence erythrose glucoside has the structure of (1,5)-glucosido-2-(1,4)-erythrose. Hence, the connecting oxygen bond occupies the 1,4 position in the initial cellobiose.

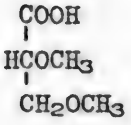
Another proof of the location of the binding oxygen bridge at the fourth carbon atom of the reducing member of the cellobiose was the perhydrol oxidation of the dimethylerythronic acid (V), synthesized by the hydrolysis of methyl hexamethylglucosido-2-erythronate (IV). This yielded dimethylglyceric acid (VI). Other dimethylerythronic acids (with the methoxy groups at the 2,3 and 2,4 positions in the molecules) could not yield dimethylglyceric acid under any circumstances.



(IV)



(V)



(VI)

It thus has been established that the biose bond in the synthesized erythrose glucoside is set up at the second carbon atom and that cellobiose possesses the structure of a (1,5)-glucosido-4-(1,5)-glucose.

EXPERIMENTAL

1. Oxidation of Cellobial

70 g of cellobial (m.p. 173-175°; $[\alpha]_D^{20}$ = + 1.2°, in water) was dissolved in 500 ml of water, and after 200 ml of a 5% solution of potash had been added, a 5% solution of potassium permanganate was added to the solution produced, with vigorous stirring and gentle heating. The permanganate solution was added until the reaction medium changed color. The glucosido-3-arabonic acid was precipitated from the filtered solution by basic lead acetate. The precipitate, after washing, was suspended in water, and the lead was thrown down with hydrogen sulfide. After the lead sulfide had been filtered out, the solution was boiled for 15 minutes to drive off the excess hydrogen sulfide, after which heating was continued in the presence of calcium carbonate. As absolute ethyl alcohol was gradually added to the filtered and concentrated solution, flakes of calcium glucosido-3-arabonate settled out. The yield was 57 g, or 71% of the theoretical.

0.0507 g substance: 0.0043 g CaO.
Found %: Ca 6.19.
$(C_{11}H_{19}O_{11})_2Ca$. Calculated %: Ca 5.77

2. Oxidation of Calcium Glucosido-3-arabonate

A mixture of 56.7 g of calcium glucosido-3-arabonate, 5 g of barium acetate, and 2.5 g of ferric sulfate was dissolved in 800 ml of water in a 1½-liter round-bottomed flask. The solution was heated to the boiling point for 15 minutes and then filtered. 100 ml of a 30% solution of perhydrol was added to the cooled filtrate, with vigorous stirring. The temperature of the reaction medium was not allowed to rise above room temperature. Three hours later, another 20 ml of perhydrol was added to the solution. After completion of the reaction, the solution was heated, then filtered, and finally evaporated under reduced pressure to minimum volume. A precipitate slowly settled out when absolute alcohol was gradually added to the condensed solution. The β-glucosido-2-erythrose thus synthesized was recrystallized from water. The yield was 26.8 g, or 58% of the theoretical. M.p. of the pure product was 149-150°; $[\alpha]_D^{20}$ = + 36.8° (in water).

0.1589 g substance: 0.2452 g CO_2; 0.1001 g H_2O.
Found %: C 42.17; H 6.98.
$C_{10}H_{18}O_9$. Calculated %: C 42.58; H 7.02.

The acetylated glucosido-2-erthyrose had a m.p. of 128-131°.

0.1522 g substance: 17.3 ml 0.1 N solution NaOH.
0.1817 g substance: 21.1 ml 0.1 N solution NaOH.
Found %: $COCH_3$ 48.77, 48.67.
$C_{22}H_{30}O_{15}$. Calculated %: $COCH_3$ 48.30.

3. Oxidation of the Glucosido-2-erythrose and Hydrolysis of the Resulting Acid

22.5 g of the glucosido-2-erythrose was dissolved in 500 ml of bromine water, and the solution produced was set aside to stand in the light, with frequent stirring for 4 days. If the solution lost its color, a few milliliters of bromine were added. The boiling solution was then neutralized with calcium carbonate. The excess calcium carbonate was filtered out, and the solution was evaporated to minimum volume. The gradual addition of absolute ethyl alcohol to the residual condensed solution caused the precipitation of flakes of calcium glucosido-2-erythronate. The precipitate was filtered out and dried at 110-120°. The yield was 19.8 g, or 71% of theory.

0.2219 g substance: 0.0221 g CaO.
0.3002 g substance: 0.0289 g CaO.
Found %: Ca 7.12, 6.90.
$(C_{10}H_{17}O_{10})_2Ca$. Calculated %: Ca 6.31.

5.2 g of calcium glucosido-2-erythronate was dissolved in 100 ml of water, and the calcium was precipitated out of the solution by the calculated quantity of oxalic acid. After the calcium oxalate had been removed, the filtrate was heated with 100 ml of 5% sulfuric acid. Then the solution was neutralized with calcium carbonate, filtered, and evaporated to minimum volume. The gradual addition of absolute ethyl alcohol to the remaining condensed solution caused flakes of calcium erythronate to settle out. The precipitate was filtered out and washed twice daily with ethyl alcohol. Then the precipitate was dissolved in 100 ml of water, and the calcium was eliminated from the solution with a calculated quantity of oxalic acid. The calcium oxalate was filtered out, and the solution was mixed with 50 ml of ethyl alcohol and evaporated to a thick syrup. The syrup was dissolved in dilute ethyl alcohol, and the solution thus prepared was evaporated to dryness. The resulting crystals of the gamma lactone of d-erythronic acid have a m.p. of 105-107° and $[\alpha]_D^{20} = -71.4°$ (in water).

The phenylhydrazide of d-erythronic acid has a m.p. of 128-130°.

According to the literature, the gamma lactone of d-erythronic acid has a m.p. of 103° and an $[\alpha]_D^{20} = -73.3°$ (in water) [3]; phenylhydrazide has a m.p. of 128° [4].

0.0921 g substance: 10.6 ml N_2 (18°, 730 mm).
0.1209 g substance: 14.1 ml N_2 (18°, 730 mm).
Found %: N 12.95, 13.15.
$C_{10}H_{14}N_2O_4$. Calculated %: N 13.28.

After the calcium d-erythronate had been removed, the solution was heated with phenylhydrazine. The precipitate that formed was filtered out and washed; the substance had a m.p. of 205-206°.

A mixed test sample with glucosazone exhibited no depression.

4. Methylation of Glucosido-2-erythronic Acid and Subsequent Oxidation of the Methylated Product

13 g of calcium glucosido-2-erythronate was dissolved in 50 ml of water, and 80 g of dimethyl sulfate was added to the solution. A solution of 25% sodium hydroxide was gradually added to the reaction mixture, with vigorous stirring, to keep the reaction mixture always slightly alkaline. Then the solution was heated to the boiling point for 10-15 minutes to decompose the excess dimethyl sulfate. The methylated product was extracted from the solution with 3 150-ml batches of chloroform. The combined chloroform extracts were washed with water and then dried and evaporated under reduced pressure to a thick syrup. The syrup was refined by vacuum distillation (10 mm, 115°). The yield was 13.7 g, or 72% of the theoretical.

c = 0.1; l = 0.5; $\alpha = -2.13°$; $[\alpha]_D^{20} = -42.6°$ (in chloroform).

0.1212 g substance: 0.4289 g AgI.
0.1471 g substance: 0.5181 g AgI.
Found %: OCH_3 46.94, 46.29.
$C_{17}H_{32}O_{10}$. Calculated %: OCH_3 46.89.

12.4 g of methyl hexamethylglucosido-2-erythronate was dissolved in 25 ml of chloroform. 200 ml of 5% sulfuric acid was added to the solution thus produced, which was then heated for 2 hours in a round-bottomed flask with a reflux condenser. The boiling solution was then neutralized with calcium carbonate. The filtered solution was evaporated to small volume. The gradual addition of absolute ethyl alcohol to the residual condensed solution caused flakes of calcium dimethyl-d-erythronate to precipitate out. The calcium salt was purified by recrystallization from hot water. The yield was 3.7 g, or 68% of the theoretical.

0.1527 g substance: 0.0212 g CaO.
Found %: Ca 10.28.
$(C_8H_{11}O_5)_2Ca$. Calculated %: Ca 10.90.

3.5 g of calcium dimethyl-d-erythronate was dissolved in 40 ml of water. 1 g of barium acetate and 0.5 g of ferric sulfate in 30 ml of water were added to the solution. The solution was then heated and filtered, after which 25 ml of 30% perhydrol was added. Three hours later, another 15 ml of perhydrol was added to the solution. After boiling for 10-15 minutes, the solution was filtered, mixed with 50 ml of bromine water, and set aside to stand in the light for 2 days. After being boiled with calcium carbonate, the solution was evaporated to minimum volume. The gradual addition of absolute ethyl alcohol to the condensed solution caused flakes of calcium dimethylglycerate to settle out.

0.1315 g substance: 0.0236 g CaO.
Found %: Ca 12.86.
$(C_5H_8O_4)_2Ca$. Calculated %: Ca 13.07.

Methyl dimethylglycerate has the following constants: b.p. 78° at 15 mm; d_4^{20} 1.0621; n_D^{20} 1.4596, which agrees with the data in the literature [2].

After the calcium dimethyl-d-erythronate had been removed, the tetramethylglucose was extracted from the solution with chloroform. The syrup left after desiccation and evaporation of the chloroform crystallized a few days later. M.p. of the pure product was 94-95°; $[\alpha]_D^{20} = +84.1°$ (in chloroform), which agrees with the data in the literature [3].

The tetramethylglucose was identified via its anilide. M.p. of the anilide was 135-136°.

SUMMARY

1. Glucosido-3-arabonic acid has been synthesized by oxidizing cellobiose with potassium permanganate.

2. The oxidation of calcium glucosido-3-arabonate by perhydrol yields glucosido-2-erythrose.

3. Glucosido-2-erythronic acid has been synthesized.

4. Hydrolysis of methylated glucosido-2-erythronic acid yields 3,4-dimethyl-d-erythronic acid and 2,3,4,6-tetramethylglucose.

5. Oxidation converts calcium dimethyl-d-erythronate into dimethyl-d-glyceric acid.

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*See CB translation p. 125 ff.

Received

SYNTHESIS OF HYDROCARBONS

VIII. REACTION OF 1,4-DICHLOROBUTYNE-2 WITH ORGANOMAGNESIUM COMPOUNDS

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In one of our previous communications [1], we described the reaction of 1,4-divinyl dichloride (1,4-dichlorobutene) with methylmagnesium bromide. It was shown that 1,4-divinyl dihalogenides can react with organomagnesium compounds, forming trans-alkenes with a centrally located double bond:

$$CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \underset{Cl}{CH_2}CH{=}CH\underset{Cl}{CH_2} \longrightarrow CH_3CH_2CH{=}CHCH_2CH_3$$

This established, for the first time, that 1,4-dihalogenides of conjugated alkaldienes, with two halogen atoms of the allyl type under the activating influence of a single double bond, behave like an allyl chloride in reactions with organomagnesium compounds.

Inasmuch as 1,4-dichlorobutene-2 proved it could exchange a halogen atom for a radical of an organomagnesium compound, the idea naturally arose of testing the feasibility of employing 1,4-dichlorobutyne-2, which is easily synthesized from butynediol, in a reaction of this sort.

There are several references in the literature to endeavors to employ 1,4-dihalogenides with a central triple bond in the synthesis of alkynes.

Thus, in an attempt to synthesize octyne-4 by the reaction of 1,4-dibromobutyne with ethylmagnesium bromide [2], a small quantity (1.2 g) of a hydrocarbon fraction, boiling in a wide temperature range (120-140°) was recovered, together with a large amount of polymers. The sole product of a reaction between 2,5-dimethyl-2,5-dichloro-3-hexyne $\left[(CH_3)_2\underset{Cl}{C}{-}C{\equiv}C{-}\underset{Cl}{C}(CH_3)_2\right]$ and methylmagnesium bromide was a solid polymer [3] instead of the expected 2,2,5,5-tetramethylhexyne-3.

The study of the reaction between 1,4-dichlorobutyne-2 and methylmagnesium bromide made in the present paper enabled us for the first time to establish beyond doubt that the chlorine atoms in the acetylenic dichloride are replaced by radicals of the organomagnesium compound. The reaction results in the formation of two isomeric hydrocarbons. One of them is the normal reaction product: an acetylenic hydrocarbon (3-hexyne) with a centrally located triple bond. The other hydrocarbon is formed as the result of a reversible allyl rearrangement of the acetylene dichloride into a diene dichloride, which takes place during the reaction; the diene dichloride reacts with the methylmagnesium bromide to form a diene hydrocarbon with a conjugated system of double bonds (2,3-dimethylbutadiene-1,3):

$$\underset{Cl}{CH_2}{-}C{\equiv}C{-}\underset{Cl}{CH_2} \longrightarrow \left[CH_2{=}C{=}\underset{Cl}{C}{-}\underset{Cl}{CH_2}\right] \longrightarrow CH_2{=}\underset{Cl}{C}{-}\underset{Cl}{C}{=}CH_2$$

$$\downarrow + 2CH_3MgBr \qquad \downarrow +2CH_3MgBr$$

$$CH_3CH_2C{\equiv}CCH_2CH_3 \qquad CH_2{=}\underset{CH_3}{C}{-}\underset{CH_3}{C}{=}CH_2$$

According to the literature [2], 1,4-dibromobutyne-2 and 1,4-di-iodobutyne-2 undergo a partial (acetylene-diene) rearrangement upon heating or standing, being transformed into 2,3-dibromobutadiene and 2,3-di-iodobutadiene, respectively, whereas 1,4-dichlorobutyne-2 proves to be completely stable, not undergoing any change even when heated with benzoyl peroxide, iodine, aluminum chloride, or zinc chloride.

It is therefore demonstrated, for the first time, in the present paper that an acetylenic dichloride – 1,4-dichlorobutyne-2, which by itself is stable – undergoes a reversible rearrangement of the acetylene-diene type when it is reacted with organomagnesium compounds:

$$\underset{\underset{Cl}{|}}{CH_2}-C\equiv C-\underset{\underset{Cl}{|}}{CH_2} \rightleftarrows \underset{\underset{Cl}{|}}{CH_2}=C=\underset{\underset{Cl}{|}}{C}=CH_2 \longrightarrow CH_2=\underset{\underset{R}{|}}{C}=\underset{\underset{R}{|}}{C}=CH_2$$

The acetylene-allene rearrangement of an acetylenic monochloride – 2-chloro-2-methylpentyne-3 — when reacted with organomagnesium compounds was first described by A.I.Zakharova [4]:

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\underset{\underset{Cl}{|}}{C}-C\equiv C-CH_3 \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C=C=\underset{\underset{Cl}{|}}{C}-CH_3 \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C=C=\underset{\underset{R}{|}}{C}-CH_3$$

EXPERIMENTAL

1. Synthesis of 1,4-Dichlorobutyne-2

1,4-Dichlorobutyne-2 was produced by gradually adding (in the course of 5 to 6 hours) thionyl chloride (130 ml) to a solution of 2-butynediol-1,4 (65 g) in anhydrous pyridine (110 ml), with chilling and mechanical stirring. The reaction mixture was decomposed with ice water the next day, and the dichloride was extracted with ether. After the ether had been driven off from the ether extract, which had been washed until it exhibited a neutral reaction (the ether extract was neutralized with anhydrous soda) and desiccated with calcium chloride, and the residue had been distilled, 1,4-dichlorobutyne-2 was recovered (a yield of 70% of the theoretical) possessing the following constants:

b.p. 80° (33 mm); n_D^{20} 1.5065; d_4^{20} 1.2575.

MR_D 29.10. $C_4H_4Cl_2$. Calculated MR_D 28.40; EM_D 0.70.

Literature data:

b.p. 68-69° (17 mm); n_D^{20} 1.5072; d_4^{20} 1.2580 [2].

2. Reaction of 1,4-Dichlorobutyne-2 with Methylmagnesium Bromide

After several attempts to react 1,4-dichlorobutyne-2 with methylmagnesium bromide, a method was developed that enabled us to achieve a fairly high hydrocarbon yield. This method is described below.

1,4-Dichlorobutyne-2 (50 g), diluted with twice its volume of absolute ether, was added during the course of 30 minutes, with constant stirring and at -16° (temperature of the reaction mixture), to methylmagnesium bromide (24 g of magnesium, 150 g of methyl bromide, and 200 ml of absolute ether). The reaction mixture was set aside to stand for 1 hour with stirring and chilling (-16°); then the temperature was raised to room temperature over the course of 30 minutes, and stirring was stopped.

The butynediol was recovered from a 30% aqueous solution by driving off the water in vacuum and then fractionating the residue. It had a b.p. of 127° (8mm) and a m.p. of 56°. The pyridine was dessicated with barium oxide and then distilled.

The next day decomposition was effected with dilute (10%) acetic acid. After the ether had been driven off (with a 1-meter Vigret dephlegmator) from the ether extract, which had been washed until it exhibited a neutral reaction and then desiccated with calcium chloride, and the residue had been fractionated, we recovered 18 g of a hydrocarbon fraction with a b.p. of 60-85° (757 mm) (cf Section 3) (yield = 54% of the theoretical), and 2.5 g of a higher-boiling fraction with a b.p. of 112-124°.

The reaction between 1,4-dichlorobutyne-2 and methyl-magnesium bromide was also carried out under other conditions: at various temperatures and various dilutions of the reaction mixture, as well as with stabilizers present to prevent polymerization of the unsaturated chlorides. The results of these experiments are listed in the table.

In Experiments 1-4, the yield of the hydrocarbon fraction proved to be considerably lower than in the experiment described below (Table, Experiment 5). In Experiment 6, performed with a small quantity (0.35 g) of pyrogallol present, we recovered, in addition to the hydrocarbon fraction (which was recovered with a good yield – 48% of the theoretical), a large quantity of the higher-boiling 112-124° fraction, which apparently was a mixture of unsaturated monochlorides, formed as a result of the replacement of one of the chlorine atoms, in the initial dichloride or in one of its isomers, by a methyl group, e.g.:

$$CH_3CH_2C{\equiv}CCH_2Cl \xleftarrow{CH_3MgBr} CH_2C{\equiv}CCH_2 \rightleftarrows$$
$$Cl \quad Cl$$

$$\rightleftarrows CH_2{=}C(Cl){-}C(Cl){=}CH_2 \xrightarrow{CH_3MgBr} CH_2{=}C(CH_3){-}C(Cl){=}CH_2$$

Thus, pyrogallol exhibited a stabilizing effect upon unsaturated monochlorides – their yield increased appreciably (up to 31% of the theoretical), while the yield of the hydrocarbon fraction dropped only slightly. As the tabular data indicate, we were able to get 80% of the initial dichlorobutyne to react with the methylmagnesium bromide in the experiment.

To check whether the 112-124° fraction contains unsaturated monochlorides with an active chlorine atom, which could be replaced by a radical when reacted with an organomagensium compound, 25 g of this fraction was reacted at room temperature with methylmagnesium bromide (8 g of magnesium and 50 g of methyl bromide in 100 ml of absolute ether). The reaction mixture was then heated for 4 hours over a water bath; decomposition was effected with dilute (10%) acetic acid. After the ether had been driven off, fractionation of the residue yielded 3.6 g of the same 60-85° hydrochloride fraction (15% of the theoretical) (cf Section 3) that was recovered when methylmagnesium bromide was reacted with the dichlorobutyne.

This proved beyond any doubt that the 112-124° higher-boiling fraction (formed in the reaction of dichlorobutyne with methylmagnesium bromide) includes an unsaturated monochloride that can again react with the methylmagnesium bromide.

An effort was made to isolate the individual monochlorides from the 112-124° fraction. Fractionation (in a tower) of 18 g of this fraction yielded two fractions with the following constants:

I. B.p. 111-113° (755 mm); n_D^{20} 1.4092; d_4^{20} 1.0060 (8 g).

II. B.p. 121.5° (755 mm); n_D^{20} 1.4597; d_4^{20} 0.9768 (6 g).

Exp. No.	Temperature, °	Reaction conditions		Yield of 60-85° hydrocarbon fraction (in % of theoretical)	Yield of 112-124° (monochloride) fraction (% of theory)	Overall yield of reaction products, based on the dichloride used
		Ml of ether per mol of CH_3MgBr	Stabilizer			
1	Room	330	–	7	–	7
2	Room	200	–	7.5	–	7.5
3	-20	450	–	15	44	59
4	-12	225	–	18	41.5	59.5
5	-16	225	–	54	8	62.0
6	-16	225	Pyrogallol	48.5	31	79.5

The first fraction, in contrast to the second, turned into tar upon standing. These fractions were not investigated any further.

3. Investigation of the Hydrocarbon Products of the Reaction of 1,4-Dichlorobutyne-2 with Methylmagnesium Bromide

Double fractionation over metallic sodium (with a column consisting of 30 theoretical trays) of 45 g of the 60-85° hydrocarbon fraction yielded 2 isomeric hydrocarbons: the normal reaction product, and acetylenic hydrocarbon with a centrally located triple bond (hexyn -3); and its isomer, a diene hydrocarbon with a system of conjugated double bonds (2,3-dimethylbutadiene-1,3).

The synthesized hexyne-3 possessed the following constants:

B.p. 80-80.5° (755 mm); n_D^{20} 1.4108; d_4^{20} 0.7268.

MR_D 28.05 (C_6H_{10} F. Calculated: MR_D 27.84)

4.370 mg substance: 14.025 mg CO_2; 4.820 mg H_2O.
6.575 mg substance: 21.105 mg CO_2; 7.260 mg H_2O.
Found %: C 87.56, 87.56; H 12.35, 12.36.
Calculated %: C 87.72; H 12.28.

Literature data:

B.p. 81° (760 mm); n_D^{20} 1.4116; d_4^{20} 0.7236 [5].

The structure of the synthesized hydrocarbon was proved by oxidation.

3 g of hexyne-3 was oxidized with 15 g of 68% nitric acid in the presence of 0.2 g of mercuric nitrate [6]. The sole oxidation product proved to be propionic acid, with a b.p. of 139° (2.2 g; yield = 40% of the theoretical), whose phenylphenacylic ester had a m.p. of 100-100.5°.

Literature data: m.p. of phenyl-phenacyl propionate is 102° [7].

The phenacyl derivative prepared by us from pure synthetic propionic acid had a m.p. of 100° (after triple recrystallization from aqueous alcohol), and a fusion test of a mixed sample of this phenacyl derivative with the phenacyl derivative of the acid synthesized by oxidizing hexyne-3 exhibited no depression.

2,3-Dimethylbutadiene-1,3, recovered together with hexyne-3 from the products of the reaction between the dichlorobutyne and methylmagnesium bromide, possessed

the following constants:

B.p. 69-69.5° (755 mm); n_D^{20} 1.4333; d_4^{20} 0.7285. MR_D 29.32.
$C_6H_{10}F_2$. Calculated: MR_D 28.97.

Literature data: B.p. 69.5-70° (772 mm); n_D^{20} 1.4392; d_4^{20} 0.7262 [3].

2.950 mg substance: 9.500 mg CO_2; 3.200 mg H_2O.
4.400 mg substance: 14.159 mg CO_2; 4.820 mg H_2O.
Found %: C 87.83, 87.81; H 12.14, 12.26.
C_6H_{10}. Calculated %: C 87.72; H 12.28.

Addition of maleic anhydride to the isolated 2,3-dimethylbutadiene-1,3 resulted in formation of a crystalline addition product, which had a m.p. of 77° after recrystallization from ligroin and desiccation (over paraffin in a vacuum exsiccator).

According to the literature, the m.p. is 78-79° [3].

A fusion test of a mixed sample of this addition product (dimethyltetrahydrophthalic anhydride) and the addition product obtained from maleic anhydride and pure 2,3-dimethylbutadiene-1,3 (from the pinacol) exhibited no depression.

Thus, investigation of the hydrocarbon fraction recovered in the reaction between 1,4-dichlorbutyne-2 and methylmagnesium bromide enabled us to establish that it included two hydrocarbons: hexyne-3 and 2,3-dimethylbutadiene-1,3.

SUMMARY

1. Study of the reaction of the 1,4-dichlorobutyne-2 with methylmagnesium bromide has enabled us, for the first time, to establish beyond a doubt that the chlorine atoms in the acetylenic dichloride are exchanged for the radicals of the organomagnesium compound.

2. It has been established that the reaction between methyl magnesium bromide and 1,4-dichlorobutyne-2 (under the conditions we have worked out for the reaction) results in the formation of a mixture of hydrocarbons, with a yield that is 54% of the theoretical.

3. Analysis of the hydrocarbon mixture has shown that it contains the normal reaction product: an alkyne with a centrally located triple bond (hexyne-3), and a diene hydrocarbon with a system of conjugated double bonds (2,3-dimethylbutadiene-1,3), the formation of which is due to a reversible allyl rearrangement of the initial dichlorobutyne.

4. It has been established that in its reaction with methylmagnesium bromide, 1,4-dichlorobutyne-2 (which by itself is stable, even when heated) undergoes a (50%) reversible allyl rearrangement (acetylene-diene), being converted into 2,3-dichlorobutadiene-1,3, which then reacts further with the methylmagnesium bromide.

5. The structure of the synthesized acetylenic hydrocarbon (hexyne-3) has been proved by its constants, by analysis, and by its oxidation to propionic acid, identified by the melting point of its phenylphenacyl ester; the structure of the diene hydrocarbon (2,3-dimethylbutadiene-1,3) has been proved by its constants, by analysis, and by synthesis of its addition product with maleic anhydride.

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Received June 21, 1948.

THE SOLUBILITY OF d-CAMPHOR IN ORGANIC SOLVENTS

M. I. Shakhparonov

Little research work has been done on the solubility of camphor. In Seidell's handbook [1], the summary of the literature data on the solubility of camphor is merely fragmentary. It was the object of our research to ascertain the link between the solubility of camphor and the dielectric constant of the solvent. V.K.Semenchenko and we have shown that many organic and inorganic compounds obey the general solubility equation very well qualitatively [2,3,4]. It was considered desirable to test this for camphor as well. Besides, data on the solubility of camphor are of interest for thier own sake.

The solvents we employed were tested, after refining, for their boiling points, densities, and refractive indexes. These tests yielded the following values:

Solvent	Boiling point, °	Density	Refractive index
Toluene.....	110.5	–	$n_D^{14.7}$ 1.4992
Carbon tetrachloride.....	76.5	–	n_D^{16} 1.4660
Acetic acid.....	m.p.16.5°	–	–
Methanol.....	64.5-65.0°	0.7940	$n_D^{15.5}$ 1.3303
Glycol.....	197.4	1.024	$n_D^{12.5}$ 1.4370
96.5% Formic Acid.....	m.p. 27°	1.2167	–

The solubility was measured visually, by the polythermic method [5], suggested by A.G.Bergman. The solid phases were not analyzed. The results are reproduced in the table and in Figs. 1, 2, and 3. Temperatures are always given in degree C. Most noteworthy are the data on the solubility of camphor in toluene and carbon tetrachloride. They indicate that certain compounds are apparently formed: (camphor)·$2C_6H_5CH_3$ and (camphor)·$2CCl_4$. This is reflected in the crystallization curves, which exhibit a maximum at low temperatures. In both cases, the composition of the solution that corresponds to the maximum is very close to the composition determined by the formulas mentioned above. The solutions whose compositions agree with these formulas are denoted by dotted lines in Figs. 2 and 3.

We were unable to establish a relationship between the solubility of camphor and the dielectric constant of the solvent. It may be supposed that this is due to the ability of camphor to form coordination compounds [3].

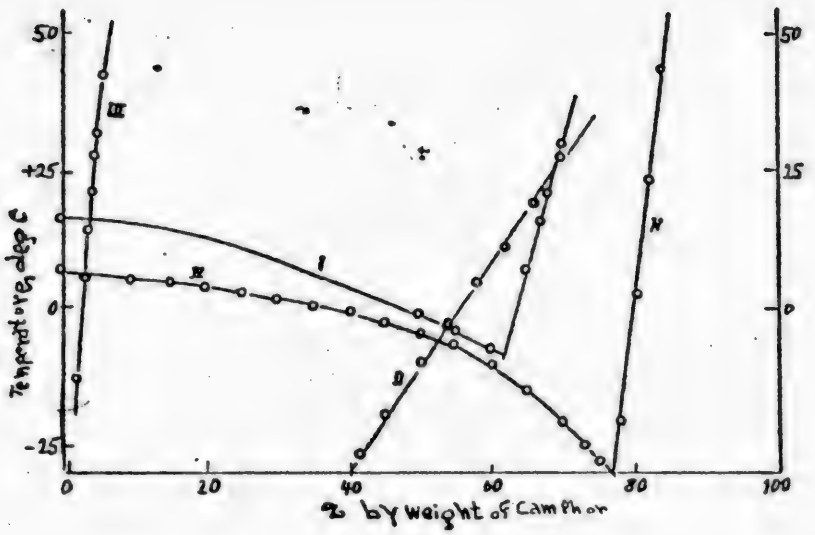

Fig. 1. Solubility of camphor: I – in acetic acid; II – in methyl alcohol; III – in glycol; IV – in formic acid.

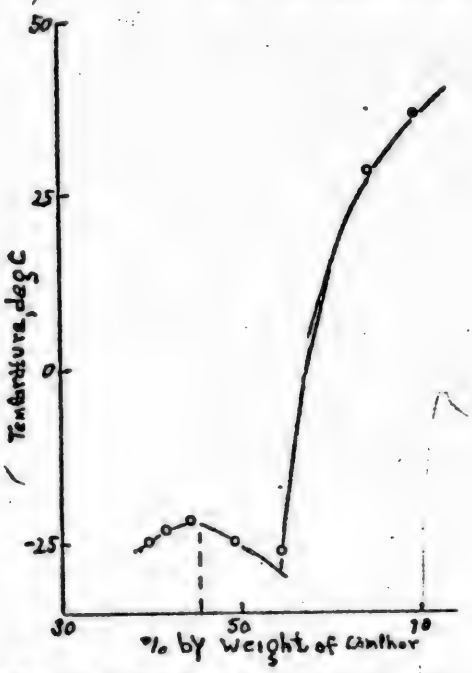

Fig. 2. Solubility of camphor in toluene.

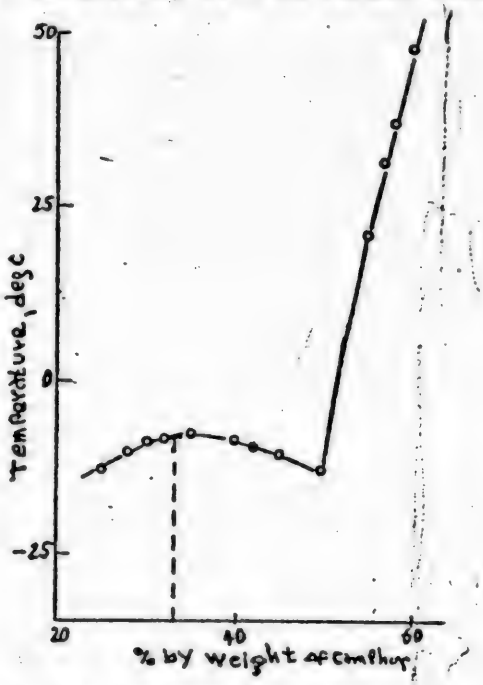

Fig. 3. Solubility of camphor in carbon tetrachloride.

SUMMARY

The solubility of camphor in toluene, carbon tetrachloride, acetic acid, methanol, glycol, and 96.5% formic acid has been investigated. The solubility curves indicate the existence of the compounds (camphor)·$2C_6H_5CH_3$ and (camphor)·$2CCl_4$.

In toluene		In CCl_4		In acetic acid		In methanol		In glycol		In 96.5% formic acid			
% camphor by weight	t° of crystallization of camphor	% camphor by weight	t° of crystallization of camphor	% camphor by weight	t° of crystallization of camphor	% camphor by weight	t° of crystallization of camphor	% camphor by weight	t° of crystallization of camphor	% camphor by weight	t° crystallization of camphor	% camphor by weight	t° crystallization of camphor
40.0	-24.8°	25.0	-13.0°°	0.0	+16.5°°°	41.2	-26.7	2.0	-13	0.0	-7.2	70.0	-20.1°°°
42.0	-28.3°	28.0	-10.3°°	80.0	- 0.9°°°	46.0	-19.3	3.0	+5.8	9.4	-5.4	73.0	-24.5°°°
45.0	-22.2°	30.0	- 9.0°°	55.0	-4.0°°°	50.0	-10.1	3.5	14.2	15.0	4.9	75.0	-27.5°°°
50.0	-24.9°	32.0	- 8.4°°	60.0	-7.1°°°	54.0	- 3.3	4.0	21.5	20.0	4.1	78.0	-18.9
55.0	-25.9	35.0	- 8.0°°	65.0	+ 7.3	58.0	+ 4.4	4.5	27.6	25.0	3.1	80.0	+ 3.1
65.0	+29	40.0	- 8.7°°	67.0	16.1	62.0	+11.5	5.0	32.2	30.0	2.1	82.0	22.7
70.0	+37	42.0	- 9.8°°	68.0	21.2	66.0	19.3	6.0	42.8	35.0	0.8	84	43.8
		43.0	-10.7°°	70.0	30.1	70.0	27.7			40.0	-0.5		
		50.0	-18.1							45.0	-2.4		
		55.0	+16.5							50.0	-4.4		
		57.0	31.8							55.0	-6.7		
		58.0	37.6							60.0	-10.1		
		60.0	48.3							65.0	-14.9		

° Crystallization of [camphor]·$(C_6H_5CH_3)_2$.

°° Crystallization of [camphor]·$[CCl_4]_2$.

°°° Crystallization of the solvent.

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Received June 21, 1949.

THE RATE OF THE AZO COUPLING OF ArX AS A FUNCTION OF THE NATURE OF THE ARYL GROUP

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In a previous paper [1] I demonstrated that the rate of the azo coupling of ArX depends upon the basicity of the X substituent; at a certain, low basicity of the substituent, the ArX compound does not couple in a qualitative test. A change in the limiting basicity at which azo coupling is observed during the conversion from one aryl group to another was also noted. Ascertaining the effect of the nature of the aryl group upon the rate of aryl coupling is of great theoretical and practical interest.

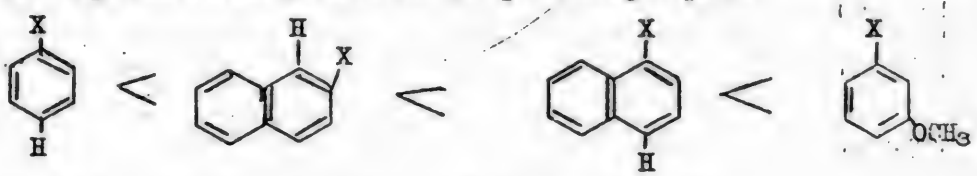
First of all, we may expect that the ease of the azo coupling of ArX should depend upon the magnitude of the oxidation potential of the corresponding quinone $Ar'O_2$. In fact, the intermediate product (the co-ordination compound formed in the reaction, Formula I):

(I)

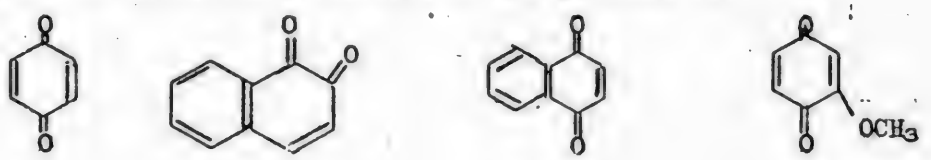
has a quasi-quinone structure; in the transition from ArX to the reaction coordination compound, the resonance of the aromatic system is disrupted about as much as it is during the transition from the hydroquinone $Ar'(OH)_2$ to the quinone $Ar'O_2$. Ar' denotes a bivalent radical – an arylene, corresponding to the aryl Ar.

In actuality, qualitatively at least, the sequence of ease of the azo coupling of ArX is found to be identical with the sequence of diminishing oxidation potentials of the $Ar'O_2$ quinones.

Thus, we may derive the following sequence of ease of azo coupling from the results of the experiments described in our preceding report:



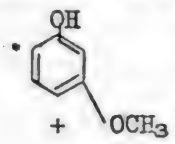
The sequence of oxidation potentials of the quinones is:



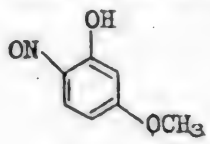
E_0 = 0.711 0.564 0.493 0.594 volt.

The 3-methoxyphenyl-substituted derivatives constitute an exception to this series: they exhibit azo coupling at a lower HX basicity than the 1-naphthyl derivatives, although the oxidation potential of 2-methoxy-1,4-benzoquinone indicates that it occupies a position in the series between 1,4-benzoquinone and 1,2-naphthoquinone.

Interpretation of this discrepancy is difficult at the present time; apparently when the orientation of two sufficiently basic groups (X and OCH_3) coincides, we must allow for the resonance forms derived from the orthoquinones and X-substituted parabenzoquinone. Furthermore, at high basicity of X, we ought to find a predominantly para coupling to X; at low X basicity (lower than that of CH_3OH or of the methoxy group), the coupling should be predominantly in the para position to the methoxy group. Since water is less basic than methanol (cf the data cited in the previous paper), in an acid medium the monomethyl ester of resorcinol (Formula II)



(II)



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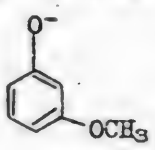


(IV)

ought to be substituted at position 6 (denoted by an asterisk), whereas in a weakly alkaline medium, in which the 3-methoxyphenolate ion (Formula IV) may be formed, azo coupling ought to occur at position 4 (denoted by a cross). This is actually what happens: According to Hodgson and Clay [2], the nitrosation of the monomethyl ester of resorcinol yields 6-nitroso-3-methoxyphenol (Formula III), whereas azo coupling with phenyldiazonium results in 4-hydroxy-3-methoxyazobenzene.

Hence, it may be thought that the dependence of the rate of azo coupling upon the oxidation potentials of the quinones is corroborated, at least qualitatively. We shall endeavor to survey the quantitative relationships. A change in the activation energy in azo coupling reactions during a transition from phenyl-substituted compounds to other aryl-substituted compounds may be assumed as approximately equal to the difference:

$$\Delta RE_{Ar'O_2} - \Delta RE_{C_6H_4O_2} = \Delta(\Delta RE),$$

where $\Delta RE_{Ar'O_2}$ is the change in the resonance energy in a transition from $Ar'O_2$, a quinone, to $Ar'(OH)_2$, a hydroquinone, and $\Delta RE_{C_6H_4O_2}$ is the change in the resonance energy in a transition from 1,4-benzoquinone to ordinary hydroquinone.

As Berliner's summary [3] indicates, the difference ΔRE approximately coincides with the difference in the changes of free energy of the hydrogenation of the quinones: $\Delta(\Delta F)$.

These data explain why coupling in the ortho position is usually observed to be less than in the para position; the activation energy of the azo coupling reaction in the ortho position ought to be 3.1 cal higher than the activation energy of azo coupling in the para position. It is possible that azo coupling in the ortho position is also hampered by the spatial proximity of the substituent.

It is difficult, however, to check the assertion that the difference between the activation energy of the azo coupling reaction of phenyl-substituted compounds and the activation energy of the azo coupling of the same substitutent with other groups equals $\Delta(\Delta F)$, inasmuch as the literature contains only isolated data on the activation energy of azo coupling reactions.

According to Conant and Peterson [9], the activation energy of the azo coupling of o-methoxyphenyldiazonium with 2-naphthol-3,6-disulfonate (R salt) averages 16.7 cal; the activation energy of azo coupling of the same diazonium salt with 1-naphthol-4-sulfonate was found to average 15.4 cal. The difference in activation energies is +1.3 cal. If we compute the difference ΔF for 1,2-naphthoquinone-4,6-disulfo acid (instead of 1,2-naphthoquinone-3,6-disulfo acid) and for 1,2-naphthoquinone-4-sulfo acid, we get + 1.5 cal.

TABLE 1

Oxidation Potentials of Quinones and Values of ΔF

$Ar'O_2$	$F_0(25°)$	ΔF cal.	$\Delta(\Delta F)$
2-Nitro-1,4-benzoquinone	0.765 [4]	34.4	+1.7
1,2-Benzoquinone	0.784	35.8	+3.1
2-Chlorobenzoquinone	0.736[8]	33.9	+1.2
1,4-Benzoquinone	0.7 [8]	32.7	0
2,5-Toluquinone	0.656 [8]	30.2	-2.5
2,5-Xyloquinone-1,4	0.597 [8]	27.5	-5.2
2,5-Thymoquinone	0.589 [7]	27.1	-5.6
1,2-Naphthoquinone	0.579 [8]	26.7	-6.0
1,4-Naphthacenequinone	0.493 [5]	22.7	-10.0
2-Methoxy-1,4-benzoquinone	0.594 [8]	26.8	-5.9
2,5-Dimethoxy-1,4-benzoquinone	0.476 [5]	21.4	-11.3
2-Hydroxy-1,4-benzoquinone	0.595 [5]	26.8	-5.9
1,2-Naphthoquinone-4-sulfonate	0.628 [5]	28.3	-4.4
1,2-Naphthoquinone-4,6-disulfonate	0.660 [5]	29.8	-2.9

TABLE 2

Activation Energy of the Azo Coupling Reaction With Diazobenzenesulfonic Acid [10].

ArX	R_{25}/R_{20}	A, Cal.	$\Delta(\Delta F)$
Dimethylaniline	1.62	+17.6	0
Dimethyl-m-toluidine	1.31	+9.8	-2.5
Diethylaniline	1.51	+15.0	0
Diethyl-m-toluidine	1.47	+14.0	-2.5
Diethyl-3-chloroaniline	1.47	+14.0	+1.2

TABLE 3

Comparison of Rates of Azo Coupling [11]

ArOH	$k_0°$	Relative velocity	$\Delta(\Delta F)$
Phenol	0.008	1	0
2-Cresol	0.01	12.5	- 2.5
3-Cresol	0.01	12.5	-2.5
2-Naphthol	0.11	137.5	-6.0
Resorcinol	0.2	250	-5.9*

According to the experiments of Goldschmidt and his associates [10], the values of the activation energy for the azo coupling reaction of amines with diazobenzenesulfonic acid may be computed from the ratios of the reaction constants at 25° and 20°.

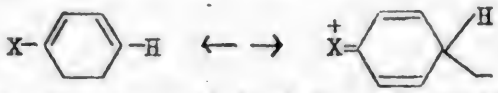
The difference between the activation energies of the azo coupling of dimethyl aniline and dimethyl-3-toluidine is +7.8 cal; the value of $\Delta(\Delta F)$ is +2.5 cal; the

*The value $\Delta(\Delta F)$ for resorcinol was adopted on the assumption that a mono ion of resorcinol is coupled; if we assume that the velocity refers to the coupling of a di ion of resorcinol, the value of $\Delta(\Delta F)$ would be much smaller, inasmuch as the 2 hydroxy-1,4-benzoquinone ion posseses a lower oxidation potential than the non-ionized compound.

difference between the activation energies of azo coupling of diethylaniline and diethyl-3-toluidine is +1 cal; the value of $\Delta(\Delta F)$ is +2.5 cal, etc. Moreover, complete coincidence cannot be expected, inasmuch as in this case the activation energy depends upon the heats of reaction of the amine salts. But it may be said that, according to Goldschmidt and Merz [11], the velocity constants of the azo coupling of phenols with diazosulfanilic acid rise as $\Delta(\Delta F)$ diminishes.

As was shown in our preceding report, 2,4-dinitrophenyldiazonium couples with: phenyl derivatives for which $pK'_{HX} \geq 1$; 1-naphthyl derivatives for which $pK'_{HX} \geq 0$; and 2-naphthyl derivatives for which $pK'_{HX} \geq 1$.

In my opinion, the HX basicity at which the azo coupling of ArX is observed during the transition from one aryl group to another (at least for simple aryls) changes as the ArX basicity does for the same aryl groups. At bottom, a diminution of the ArX basicity in the transition from one aryl to another indicates the high probability of resonance.



It may, therefore, be supposed that the probability of the appearance of a negative charge on the carbon atom increases as the basicity of the X group diminishes. So simple a line of reasoning is valid, apparently, for only the simplest aryls. It is inapplicable to aryl groups possessing additional activating groups (with unshared pairs of electrons besides X, as in the 3-methoxyphenyl radical).

Let us compare, by way of example, the change in basicity during the transition from phenyl derivatives to 1- and 2-naphthyl derivatives.

TABLE 4

X	$pK'(C_6H_5X)$	$pK'(1\text{-}C_{10}H_7X)$	$pK'(2\text{-}C_{10}H_7X)$
$-NH_2$	4.58 [12]	3.92 [12]	4.11 [12]
$-NHCH_3$	4.85 [12]	3.70 [12]	
$-NHC_2H_5$	5.11 [12]	4.24 [12]	

Differences: $pK'(C_6H_5X) - pK'(1\text{-}C_{10}H_7X) = 0.91$ (average);

$pK'(C_6H_5X) - pK'(2\text{-}C_{10}H_7X) = 0.47$.

The qualitative coincidence of these differences with the basicity differences for pK_{HX}, for which azo coupling was observed (vide supra).

If a single ArX compound can be coupled at two quinogenic points, an endeavor may be made to compute the ratio of the quantities of isomers thereby produced.

1. Azo coupling of phenol. Phenol couples with a hydroxyl group in the ortho and para position. From what has been set forth above, the ratio of the velocity constant of ortho substitution to that of para substitution is:

$$\frac{k_o}{k_p} = \frac{2P_o}{P_p}\, e^{-\frac{\Delta(\Delta F)}{RT}},$$

where P_o and P_p are the probability coefficients in the expression for the velocity constant of substitution at the ortho and para positions, respectively. Taking as a

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*The factor 2 appears as a result of the presence of two ortho positions and one para position.

first approximation $P_o \approx P_p$, and inserting numerical values, we get:

$$\frac{k_o}{k_p} = 2e^{-\frac{3100}{RT}} = 0.0106 \ (25°C).$$

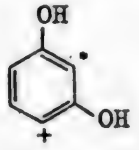
In other words, the quantity of the ortho derivative formed should be only 1% of that of the para derivative. According to Bamberger, about 1% of 2-hydroxyazo benzene is obtained in the azo coupling of phenyldiazonium with phenol [13].

2. Azo coupling of 1-naphthol. This takes place at positions 2 and 4. At 25° C the ratio of the constants is:

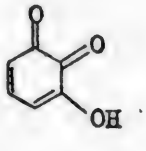
$$\frac{k_2}{k_4} = e^{-\frac{4000}{RT}} = 0.0025.$$

According to Fierz [14], less than 1% of ortho oxyazo dyes is synthesized when 1-naphthol is coupled with ordinary diazonium.

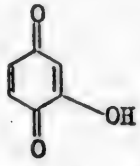
3. Resorcinol couples in position 2 (denoted by an asterisk) and in position 4 (denoted by a cross: Formula V).



(V)



(VI); E_o=0.677



(VII); E_o = 0.597

The value of E_o is 0.677 (Formula VI) and 0.597 (Formula VII) for the respective quinones. Whence $\Delta(\Delta F) \neq 3700$ cal.

The ratio of the velocity constants is:

$$\frac{k_2}{k_4} = \frac{1}{2} e^{-\frac{3700}{RT}} = 0.001.$$

According to this calculation, the quantity of the 2-substitution product obtained is about 2% or so of the quantity of the 4-substitution product. According to Pukall [15], the quantity of 2-phenylazoresorcinol recovered is about 5% of the aggregate quantity of azo dye obtained when phenyldiazonium is coupled with resorcinol. The coincidence of the computational results with the experimental data might be better if it were assumed that a resorcinol di-ion is coupled.

The cited experimental data coincide with the computed results at least in order of magnitude. But the ratio of the quantities of isomers in this computation (bearing in mind merely the difference in the resonance energies of the quinones) ought not to change in a transition from one substituent to another. Nor is this ever observed to happen. Steric hindrances play a definite part in such substituents as chlorine and the dimethylamino group; but it seems that we cannot attribute a change in the isomer ratio to steric factors alone.

The fact of preponderant substitution in the ortho position in some reactions is worthy of note. Thus, with slightly active diazoniums, 1-naphthol couples chiefly at position 2 [14]; according to Kolbe, the carboxylation of phenol and 1-naphthol yields ortho hydroxycarboxylic acids. In the case of slightly active agents it may be assumed that the resonance form with a high energy content, namely, the ortho resonance form, reacts, or, more precisely, the probability of this form increases

in the excited state with high energy. Possibly this is the reason for the observed change in the ratio of the quantities of ortho and para substitution products.

SUMMARY

1. The rate of azo coupling of ArX is related to the magnitude of the oxidation potential of the corresponding $Ar'O_2$ quinone; the rate of azo coupling rises as the oxidation potential of the quinone decreases.

2. As far as we can see, the difference in the activation energies of the azo coupling reaction of two types of aryls coincides or is close to the difference in the changes of free energy in the hydrogenation of the quinones.

3. The basicity of HX at which the azo coupling of ArX occurs changes in a transition from one aryl to another as the basicity of ArX changes for the same aryls.

4. An endeavor has been made to calculate the relative quantities of isomers produced in an azo coupling reaction.

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Received June 21, 1948.

CONDENSATION OF VINYL ETHERS AND α-CHLOROETHERS WITH BENZENE

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In connection with our researches on the condensation of acetylene with aromatic compounds [1], we undertook a study of analogous reactions with vinyl ethers. Numerous instances of the condensation of various ethylene compounds with aromatics have been described in the literature; they usually take place readily in Friedel-Crafts syntheses [2].

But in such reactions of the vinyl ethers, their sepcific peculiarities, described in detail in the research work of M.F.Shostakovsky [3], must be taken into account. Of particular importance in our reactions are the ease with which vinyl ethers are polymerized in the presence of acids and halides and their tendency to convert into oxonium coordination compounds (as with HCl, for example), that are tautomeric with alpha chloroalkyl ethers.

Obviously, the first thing to be considered in choosing our conditions for the benzene condensation is the possibility of polymerization of the vinyl ethers.

We solved a similar problem at an earlier date [1], when in perfecting the condensation of styrene with benzene, we succeeded – contrary to some assertions in the literature – in synthesizing 1,1-diphenylethane; these condensations were effected under the mildest possible conditions. On the other hand, the possibility of the vinyl ethers being converted into alpha chloro ethers, which then enter into reaction with the benzene must be borne in mind; we therefore did not confine ourselves to a study of reactions with the vinyl ethers, but also investigated the reactions with the corresponding alpha chloro ethers.

At the moment we completed our experiments in this research project there appeared an article by V.V.Korshak and his coworkers [4], in which they reported the results of their investigation of condensations of vinyl butyl ether with benzene in the presence of $AlCl_3$. These condensations were effected by heating over a water bath and adding the vinyl ether (50 g) to all the $AlCl_3$ (34 g) in benzene (120 g). The authors did not isolate any condensation products; they recovered only a polymer of the vinyl ether and some butylbenzene.

Comparing these results with those secured by us, we reached the conclusion that the condensation conditions evolved by V.V.Korshak were unsuitable: they are too harsh. Our condensations were effected by carefully adding small batches (1-2 g) of $AlCl_3$ to a mixture of vinyl butyl ether in an excess of benzene; the mixture was stirred constantly, with its temperature kept at no more than 27° by chilling. Under these conditions noticeable yields of α-phenyl butyl ether (some 20% of the theoretical) and of n-butylbenzene (some 30% of the theoretical) were recovered, although the vinyl ether was partially polymerized.

In a series of tests we found that an excess of $AlCl_3$ (more than 1.5 mols), or heating while the $AlCl_3$ is added, causes the polymerization process to predominate. The condensation reaction may take place as a result of the mixture of the reagents with $AlCl_3$ being allowed to stand at room temperature.

Our efforts to substitute one of the other customary condensing agents for the $AlCl_3$ were fruitless. The vinyl butyl ether was completely polymerized when we used H_2SO_4, H_3PO_4, or $SnCl_4$, even at low temperatures. We then proceeded to examine the condensations of benzene with α-chloroethyl butyl ether. This ether was synthesized by saturating either vinyl butyl ether (by the method worked out by M.F. Shostakovsky and A.V.Bogdanova [5]) or a mixture of acetaldehyde and n-butyl alcohol [6] with HCl. Both of these chloro ethers proved to be identical, nor did they manifest any differences in condensation.

The literature is replete with references to condensations of alpha chloro ethers with aromatic compounds. High activity of the chlorine atom is usually noted, together with a parallel ready breaking of the ether bond. Such condensations usually result in 1,1-diphenyl alkanes when $AlCl_3$ is employed [7].

The well-known chloromethylation (or chloroalkylation) reaction can be effected with the alpha chloro ethers, as well as with the corresponding aldehydes, and HCl by heating in the presence of $ZnCl_2$, $SnCl_4$ or acids [8]. It has been noted [9] that chloromethyl ether reacts in two ways, depending on the catalyst present: yielding benzyl chloride benzyl methyl ether.

When we condensed α-chloroethyl butyl ether with benzene in the presence of $AlCl_3$, we obtained a yield of as much as 55% of the theoretical of α-phenyl ethyl butyl ether.

As we found no description of α-phenyl ethyl butyl ether in the literature, we synthesized it from phenylmagnesium bromide and dibutylacetal by Chichibabin's method [10]. The synthesis conditions were modified in accordance with Chichibabin's statement that he had been unable to synthesize this ether. Repeated condensations of a-phenyl ethyl butyl ether with benzene under more severe conditions (100-120°; 2 mols of $AlCl_3$) yielded 1,1-diphenylethane; n-butylbenzene, and 9,10-dimethylanthracene.

One of our endeavors to condense α-chloroethyl butyl ether with benzene yielded nothing but dibenzyl, with a yield that was 32% of the theoretical. Endeavors to condense α-chloroethyl butyl ether with benzene under conditions that resembled those in chloroalkylation reactions with $ZnCl_2$ and HCl present and with heating, or with $SnCl_4$, indicated an appreciable percentage of chlorine-containing compounds, most likely α-chloroethylbenzene, their aggregate yield being low. In this case, evidently, the excess of HCl and the heating cause the oxonium form of the alpha chloro ether to break down at the ether bond, as reported by Shostakovsky; since the catalysts employed ($ZnCl_2$ or $SnCl_4$) are unable to activate the benzene hydrogen sufficiently, the reaction is not at all thoroughgoing, and its yields are poor.

If these considerations were correct, we might expect that the replacement of benzene by aromatic compounds with more active ring hydrogen would make it possible to effect such condensations more easily and with higher yields.

We condensed vinyl ethyl ether, saturated with HCl, with anisole. A preliminary experiment established that pure α-chlorodiethyl ether, prepared from vinyl ethyl ether, does not react with anisole, even upon long standing. A mixture of vinyl ethyl ether with anisole was saturated with HCl, at -10° at first, and then at 0°. This resulted in the synthesis of α-chloroethylanisole and dianisylethane; the mixture apparently contained some α-anisyl ethyl ether as well.

EXPERIMENTAL

The vinyl ethers, procured from M.F.Shostakovsky, whom the authors wish to thank for his kindness, were carefully purified; they possessed, after fractionation over sodium, constants that accorded with those reported in the literature [3]

We prepared the aluminum chloride from pure aliminum and HCl; at times we used the commercial product. Condensation was effected in a three-necked flask fitted with a reflux condenser and a stirrer. The addition of the $AlCl_3$ took 3 to 5 hours. The condensation products were recovered as is usually done in Friedel-Crafts syntheses. A few examples of condensation are listed below.

1. Vinyl Butyl Ether – Benzene

Used: 10 g of vinyl butyl ether, 100 ml of benzene, and 14 g of $AlCl_3$; the mixture stood for 84 hours at 13°.

Recovered: 4.5 g of n-butylbenzene (33% of the theoretical); 3.5 g of α-phenyl ethyl butyl ether (20% of the theoretical); and 4 g of a tarry polymer.

2. α-Chloroethyl Butyl Ether – Benzene

Used: 10 g of the chloroethyl butyl ether, 100 ml of benzene, and 15 g of $AlCl_3$ (added in the course of 2.5 hours); the mixture stood for 12 hours at 25°.

Recovered: 7 g of α-phenyl ethyl butyl ether (54.5% of the theoretical); 0.5 g of high-boiling substances; and 1 g of a tarry polymer.

3. α-Phenyl Ethyl Butyl Ether – Benzene

Used: 10 g of α-phenyl ethyl butyl ether; 50 ml of benzene; 11.2 g of $AlCl_3$; the mixture was heated for 2.5 hours over a boiling water bath.

Recovered: 2 g of n-butylbenzene (27% of the theoretical); 4 g of 1,1-diphenylethane (39% of the theoretical); and 1 g (9%) of 9,10-dimethylanthracene.

n-Butylbenzene: b.p. (730 mm) 178-180°; d_4^{20} 0.8607; n_D^{20} 1.4896; MR 45.01 (calculated: 44.78).

Oxidation in sealed ampoules with HNO_3 yielded benzoic acid, with a m.p. of 121°. Nitration, reduction, and acetylation of the amine yielded an acetamino derivative, with a m.p. of 105° [12].

1,1-Diphenylethane: b.p. (720 mm) 260-262°; n_D^{20} 1.5704. Oxidation by chromic anhydride in acetic acid yielded benzophenone [1].

9,10-Dimethylanthracene: yellow crystals from alcohol. M.p. 178°. Oxidation yielded anthraquinone. A mixed test fusion sample with the known product exhibited no depression [1].

α-Phenyl Ethyl Butyl Ether

Synthesis from dibutylacetal: 52 g of C_6H_5Br, 8 g of Mg and 200 ml of ether were used. After all the magnesium had dissolved, the ether was driven off; 24 g of dibutylacetal was added to the residue from a dropping funnel over the course of 2 hours while the mixture was heated to 100-200°. The mixture was then heated to 120° for another half hour, after which it was cooled, decomposed with water, and extracted with ether. This yielded 21.5 g of a substance with a b.p. of 220-230°. Refractionation yielded 16 g (65.5% of the theoretical) of a pure product with a characteristic ethereal odor.

B.p. (730 mm) 220-222°; d_4^{20} 0.9063; n_D^{20} 1.4832; MR 56.10 (calculated 55.54)

0.1776 g substance: 0.5242 g CO_2; 0.1570 g H_2O.

Found %: C 80.49; H 9.82.

$C_{12}H_{18}O$. Calculated %: C 80.89; H 10.11.

The product recovered in the condensations:

B.p. (730 mm) 220-222°; d_4^{20} 0.9057; n_D^{20} 1.4832; MR 56.15.

0.1446 g substance: 0.4245 g CO_2; 0.1382 g H_2O
Found %: C 80.64; H 10.61.
$C_{12}H_{18}O$. Calculated %: C 80.89; H 10.11.

4. Vinyl Ethyl Ether – Anisole

Used: 10 g of vinyl ethyl ether and 10 g of anisole, a current of anhydrous HCl (1.5 g increase in weight) was passed through at -10°; then HCl was passed through for another 45 minutes at 0°. The mixture turned red . 7.2 g of a mixture of products was recovered by treatment with ice and extraction with ether. Distillation of this mixture yielded the following substances:

α-Chloroethylanisole (2.4 g): b.p. (12 mm) 60-65°. HCl was split off by heating to 115° for 6 hours with pyridine. This yielded vinylanisole, b.p. (16 mm) 91-95°; n_D^{20} 1.5152; it contained no halogen; it decolorized bromine strongly [14].

The second fraction (0.8 g), with a b.p. (12 mm) of 95-100°, had the characteristic odor of anise, and probably was α-(methoxyphenyl)-diethyl ether.

The third fraction, with a b.p. (15 mm) of 215-217°, was 3.0 g of 1,1-dianisylethane; it crystallized completely. M.p. 70-71° [14].

Anomalous Condensation of α-Chloroethyl Butyl Ether (II) with Benzene

Used: 14 g of α-chloroethyl butyl ether, 100 ml of benzene, and 18 g of $AlCl_3$ (added in the course of 3 hours at 25°); the mixture was allowed to stand for 80 hours at 20-25°. It received the customary treatment. Fractionation yielded a fraction with a b.p. (6 mm) of 130-140°, all of which crystallized in the receiver. M.p. 51-52°.

0.1028 g substance: 0.3466 g CO_2; 0.0712 g H_2O.
Found %: C 92.50; H 7.75.
$C_{14}H_{14}$. Calculated %: C 92.25; H 7.75.

A test sample mixed with pure dibenzyl exhibited no depression of the melting point.

SUMMARY

1. In the presence of $AlCl_3$ vinyl butyl ether condenses with benzene, yielding α-phenyl ethyl butyl ether and n-butylbenzene.

2. When α-chloroethyl butyl ether is condensed with benzene in the presence of $AlCl_3$, the sole product is α-phenyl ethyl butyl ether, with a yield of up to 55% of the theoretical.

3. In the presence of an excess of $AlCl_3$ α-phenyl ethyl butyl ether condenses with benzene when heated, forming n-butylbenzene, 1,1-diphenylethane, and 9,10-dimethylanthracene.

4. When acted upon by an excess of HCl with no halogen salts present, vinyl ethyl ether readily condenses with anisole, the principal products being α-chloroethylanisole and 1,1-dianisylethane.

5. The synthesis of α-phenyl ethyl butyl ether from dibutylacetal and phenyl magnesium bromide has been worked out (65% of the theoretical yield).

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Received June 25, 1948.

HALOGEN DERIVATIVES OF CYCLIC α-DIKETONES

I. THE STRUCTURE OF THE HALOGEN DERIVATIVES OF 1,2-CYCLOPENTANEDIONE

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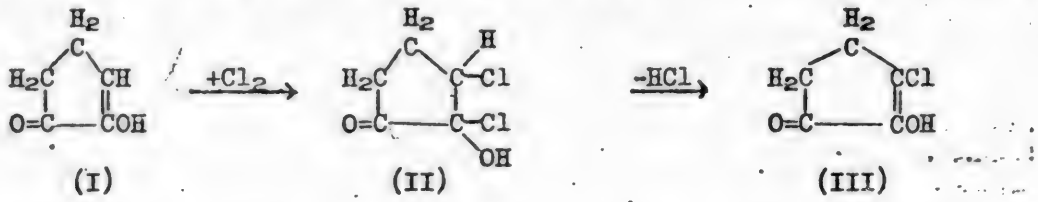
Setting as our goal the study of the conversions of cyclic α-diketones during dehalogenation and the ascertaining of the feasibility of utilizing such reactions in synthesis, we thought it necessary first of all to clear up some uncertain factors concerning the formation and the structure of the halogen derivatives themselves.

Little work has been done on the halogen derivatives of 1,2-cyclopentanedione, in particular, but it seemed that the course of the reaction might be predicted from the properties of the diketone. It is known that cyclic α-diketones differ from the aliphatic in that they possess marked acidic properties and tend to react in the enol form; the acidic properties of halogenized cyclopentanedione are even more marked [1]. There is every reason to believe that 1,2-cyclopentanedione reacts with a halogen as cyclopentanone [2] does, adding a halogen molecule at the double bond of the enol group.

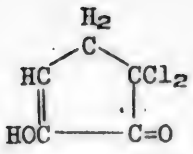
The saturated dihalogen derivative of the keto alcohol formed as a result of this reaction is unstable and gradually liberates a hydrogen halide, forming a monohalogen derivative of the diketone in its enol form:



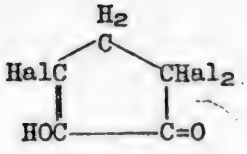
This reaction diagram explains the fact, already noted by Dieckmann [1], that when cyclopentanedione is chlorinated, crystals of the monochloro derivative are seen to settle out only after the reaction mixture has stood for some time and that crystallization is speeded up by heating the solution (after chlorine has been passed through). Obviously, heating facilitates the decomposition of the unstable dihalogen derivative of the keto alcohol.

According to this diagram, it must be supposed that as chlorination continues, a second halogen molecule is added at the double bond (III), forming an unstable trichloro derivative of the keto alcohol, which in turn splits off HCl to form an asymmetrical dichloro derivative (IV).

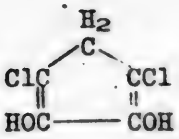
Dieckmann did not synthesize dihalogen derivatives of this sort, merely obtaining trihalogen derivatives in the enol form (V), which were formed, as we see it, as the result of a further reaction of the dihalogen derivative according to the same diagram.



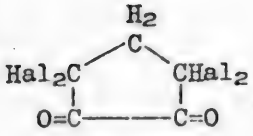
(IV)



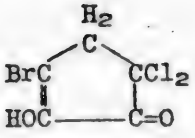
(V)



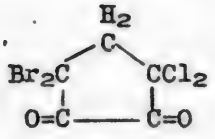
(VI)



(VII)



(VIII)



(IX)

We proved to our own satisfaction that under certain conditions dihalogen derivatives can also be produced. By chlorinating cyclopentanedione without external chilling, for example, we produced dichloro derivatives, although the weight of chlorine absorbed was equivalent to 1 mol. It must be supposed that in a warm solution, the intermediate compound (II) breaks down quickly, and, inasmuch as the monochloro derivative is a stronger acid than the initial diketone, the reaction velocity of the addition of chlorine to the double bond of the monochloro derivative will be higher than when it is added to the double bond of the ubsubstituted diketone. In this case, of course, half of the diketone does not enter into reaction, but remains unchanged. We synthesized the same dichloro derivative by the careful chlorination of the monochloro derivative in the cold, using 1 mol of chlorine.

Our dichloro derivative of cyclopentandione proved to be identical with the compound synthesized by Hantzsch as the product of the decomposition of trichlorocyclopentendihydroxycarboxylic acid [3] and described by him as dichloro-1,3-diketopentamethylene. In reducing his dichloro derivative, Hantzsch synthesized the corresponding monochloro derivative. Dieckmann proved that Hantzsch's monochloro derivative was identical with the chlorine derivative of 1,2-cyclopentanedione (III) and, hence, possesses a 1,2-diketone structure instead of a 1,3 structure.

As for the dichloro cyclopentanedione, both an asymmetrical structure (IV) and a symmetrical structure are conceivable. But then we must expect the di-enol form (VI), by analogy with the 3,5-dicarboxylic esters of the 1,2-cyclopentanediones. We know that both the 3-monocarboxylic ester and the monochloro derivative titrate like dibasic acids [4]. We have established that dichlorocyclopentanedione titrates like a monobasic acid and, hence, must have an asymmetrical structure.

Comparing the work of Dieckmann with that of Hantzsch, we find a contradiction in the properties attributed by them to polyhalogen derivatives of cyclopentanedione. Dieckmann proved that monohalogen derivatives of 1,2-cyclopentanedione (III) react with chlorine or bromine in two stages. First, a trihalogen derivative (V), which (like the monohalogen derivative) has an enol structure, is formed; it is colored by ferric chloride, titrates like a monobasic acid, and does not liberate iodine from a solution of potassium iodide. As we noted above, a dihalogen derivative (IV) may be synthesized under certain conditions. In the second stage, a tetrahalogen derivative (VII) is formed, which does not have an enol form and reacts like a hypobromite. Accordingly, we must assume that dichloro-1,2-cyclopentanedione will also react with a halogen in two stages. In the first stage, the enol form of a trihalogen derivative

must be formed, and a tetrahalogen derivative, which reacts like a hypobromite, in the second stage. When Hantzsch brominated dichloropentanedione, however, he obtained a product that he described as monobromodichlorocyclopentanedione, which was not colored by ferric chloride and did liberate iodine from a solution of potassium iodide. It seemed to us that, with such properties, the substance described by Hantzsch could only be a dibromodichloro derivative.

We therefore checked the bromination reaction of dichlorocyclopentanedione (IV), finding that the reaction actually took place in two stages. In the first stage, we recovered a new substance, which was colored intensively by ferric chloride and titrated like a monobasic acid. Its equivalent and its elementary analysis corresponded to that of monobromodicylorocyclopentanedione (VIII). Its melting point was 30° above the melting point given by Hantzsch. Continuing the bromination with care, we synthesized another individual substance, which was not colored by ferric chloride and liberated iodine from a solution of potassium iodide in the cold.

We therefore believe that this substance has the structure (IX). The melting point of this substance is only two degrees above the melting point given by Hantzsch for his monobromodichlorocyclopentanedione. This confirms our conjecture that Hantzsch's product actually was a dibromodichloro derivative.

EXPERIMENTAL

1. Chlorocyclopentanedione (III)

(3-Chlorocyclopenten-2-ol-1-one)

Chlorine was passed through an externally chilled solution of 4.7 g (0.048 mol) of the cyclopentanedione* in 40 ml of water until the increase in weight totaled 3.5 g (0.05 mol). Three hours later crystals of the monochloro derivative began to settle out. The next day the crystals were filtered out and recrystallized from hot water. The yield was 3.7 g (58% of the theoretical). Long, colorless needles with a m.p. of 137-138°, i.e., corresponding to the description in the literature [1]. Ferric chloride turned it claret.

2. Dichlorocyclopentanedione (IV) (2,2-Dichlorocyclopenten-5-ol-1-one)

The chlorination of the cyclopentanedione was effected as described above, but without external chilling, so that the temperature rose to 50-60°.

Used: 4.9 g (0.05 mol) of the cyclopentanedione and 3.5 g (0.05 g) of chlorine. The yield was 3.5 g (41% of the theoretical). Colorless prisms with a m.p. of 118-119°, which corresponds to the data given by Hantzsch for 2,2-dichloro-1,3-cyclopentanedione [3]. It turns claret-colored with ferric chloride. It titrates like a monobasic acid.

We synthesized the same product by carefully chlorinating monochlorocyclopentanedione with external chilling, as well as from phenol by Hatzsch's method [3].

0.1486 g substance: 8.40 ml 0.1 N NaOH.

Found : M 177.

$C_5H_4O_2Cl_2$. Calculated : M 167.

3. Monobromodichlorocyclopentanedione (VIII)

(4-Bromo-2,2-dichlorocyclopenten-5-ol-1-one)

Bromine water was added a drop at a time to 0.33 g of the dichlorocyclopentanedione until the instantaneous bleaching ceased. The solution was then evaporated over a water bath down to a small volume and set aside to crystallize. The crystals that settled out were filtered out and recrystallized from hot water. The yield was 0.29 g (53% of the theoretical). Colorless needles with a m.p. of 103°. It is

*1,2-Cyclopentandione was prepared, with sligh modifications, by the Jaeger method [6] the yield being 54% of the theoretical.

turned claret-colored by ferric chloride, does not liberate iodine from a solution of potassium iodide, and titrates like a monobasic acid.

0.0782 g substance: 3.24 ml 0.1 N NaOH.
0.0527 g substance: 2.07 ml 0.1 N NaOH.
Found: M 241, 254.
$C_5H_3O_2Cl_2Br$. Calculated: M 245.9.

Analyses of the halogen content gave figures that were somewhat low, closely corresponding to a content of one molecule of water of crystallization, though neither the melting point nor the halogen percentage changed appreciably after vacuum sublimation.

7.47 mg substance: 13.45 mg of silver halide; 12.22 mg AgCl.
11.88 mg substance: 21.78 mg of silver halide; 19.74 mg AgCl.
Found %: Br 29.59, 30.89; Cl 27.31, 27.44.
$C_5H_3O_2Cl_2Br$. Calculated %: Br 32.49; Cl 28.83.

Though the analytical data cannot be considered fully satisfactory, they justify the assumption that the compound in question contains two chlorine atoms and only one bromine atom.

4. Dibromodichlorocyclopentanedione (IX)

(5,5-dibromo-3,3-dichloro-1,2-cyclopentanedione)

Bromine water was added to 0.32 g of the monobromodichlorocyclopentanedione until instantaneous bleaching ceased, after which the reaction mixture was treated as indicated above. The yield of the dibromodichlorocyclopentanedione was 0.15 g (38% of the theoretical).

It crystallizes from water as colorless platelets, with a m.p. of 69-70°, which become white and amorphous after standing in an exsiccator, evidently due to the loss of the water of crystallization. It is not colored by ferric chloride, and it liberates iodine from a solution of potassium iodide. All its properties indicate that it corresponds to the product described by Hantzsch [3] as monobromodichlorocyclopentanedione; m.p. 67° (not sharp).

SUMMARY

1. When 1,2-cyclopentanedione is chlorinated and brominated, the halogen replaces, in stages, 4 atoms of hydrogen located in the alpha position to the two carbonyl groups; this results in the formation of mono- and asymmetrical di-, tri-, and tetrahalogen derivatives.

2. The mono-, di-, and trihalogen derivatives of cyclopentanedione possess an enol form and are titrated like monobasic acids.

3. The tetrahalogen derivative of cyclopentanedione has no enol form and reacts like a hypobromite.

4. The product described by Hantzsch as monobromodichlorocyclopentanedione is dibromodichlorocyclopentanedione.

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Received June 27, 1948.

THE BETAINELIKE COMPOUNDS FORMED WHEN A PROTON IS DETACHED FROM THE NH GROUP

IV. BETAINE AZENIATES OF THE QUINOLINE SERIES *

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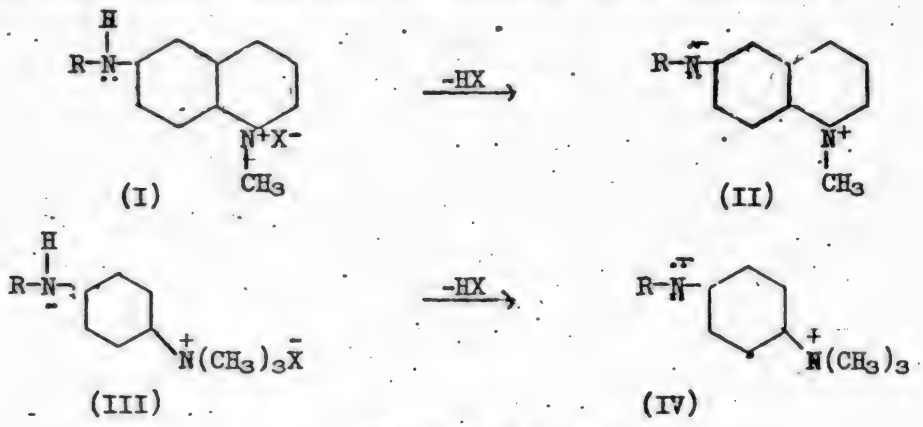
In our preceding report [1] we came to the conclusion that betaine azeniates ought to be readily formed from quaternary salts when the dissociability of the hydrogen in the NH group is increased, and the possibility of stabilizing the betaine formed is dependent upon the mesomeric shift of electrons from the azeniatic N atom. It follows that a change in the system's bonds to the NH group in the direction of strengthening their electrophilic nature ought to facilitate the formation of betaines.

To test this statement, we set up experiments on the synthesis of betaine azeniates of the quinoline series of structure (II, a - c). These compounds differ from the betaines previously studied in that the azeniatic N atom is not attached to the benzene ring, which has an ammonium group, but to the methyl quinolinium group, which is more highly electrophoric. Hence, it might be thought that these betaine azeniates will be formed much more easily than the compounds of the benzene series with a similar structure (IV, a - c).

The experimental data have corroborated this conclusion:



(I) (II) (III) (IV)

X = n-$CH_3C_6H_4SO_3$, I

(a) R = 2,4,6-trinitrophenyl (picryl)
(b) R = 2,4-dinitrophenyl
(c) R = n-toluenesulfonyl

Though a large number of phenol betaines of the quinoline series [7] is known, there has been no description of betaine azeniates of this class in the literature up to this time. Only in Meigen's paper [2] do we find a statement that when an alkali acts upon the iodomethylate

* Part of the material in this communication has been reported to the scientific conference of the Moscow Textile Institute in January 1947 (cf Theses and Reports of the Conference of the Moscow Textile Institute, p. 149, Moscow, 1947).

of 4-(2',4'-dinitroanilino)-quinoline, a purple product is formed, to which the author, without analyzing it, attributes the structure of a base. Only of late have there appeared a limited number of descriptions of betaine azeniates, containing other heterocyclic rings [3].

The properties of the compounds we have synthesized (the possibility of readily converting them into the initial quaternary salt, their deep color, their inability to dissolve in nonpolar solvents), the data of analysis, and their resemblance to the phenol betaines of the quinoline series enables us to consider the betaine structure (II) of these substances established.

The formation of a betaine of the structure (II, a) in which the azeniatic N atom links two systems possessing a marked mesomeric effect, is easiest of the compounds of this series (II). This compound rapidly settles out as a claret-colored precipitate when as weak an alkali as pyridine acts upon an aqueous solution of the methyl-p-toluene sulfonate of 6-picrylaminoquinoline (I,a). Under these conditions the aqueous solution of the quaternary salt of the benzene series (III, a) [4] does not yield a betaine, but merely turns red.

Nor is a betaine azeniate of the structure (II, b), containing a dinitrophenyl group instead of picryl, formed under the action of pyridine. It is formed when ammonia or soda acts upon the quinoline salt (I,b). The corresponding derivative of the benzene series (IV, b) is formed only by the action of caustic soda [5].

The action of ammonia or soda upon an aqueous solution of a quinoline salt of structure (I,c), containing an n-toluene sulfonyl radical, causes an orange precipitate to settle out, which readily loses two molecules of water, turning into a red betaine azeniate (II, c). Here, too, the presence of the quinoline ring facilitates betainization.

Thus, in all three cases (a, b, and c), betaine azeniates of the quinoline series, containing a strongly electrophilic methylquinolinium group, are formed more readily than the corresponding compounds of the benzene series, which supports the assertion made above. In accordance therewith, the ease of formation of betaine azeniates varies with the structure of the R group attached to the azeniatic N atom; it diminishes as follows for both series of compounds (II and IV): picryl, 2,4-dinitrophenyl, and p-toluene-sulfonyl.

EXPERIMENTAL

The Methyl-p-toluene Sulfonate of 6-(2',4'-Dinitroanilino)-quinoline (I, b).

This compound was prepared by fusing 6-(2',4'-dinitroanilino)-quinoline with methyl p-toluene sulfonate at 140°. Bright yellow crystals (from dilute alcohol) with a decomp. temp. of 242-242.5° (the capillary was placed in the instrument at 230°).

0.2125 g substance: 0.1001 g $BaSO_4$ (Carius).
0.2246 g substance: 0.1041 g $BaSO_4$.
Found %: S 6.47, 6.37.
$C_{23}H_{20}O_7N_4S$. Calculated %: S 6.46.

The initial 6-(2',4'-dinitroanilino)-quinoline [2] was prepared by heating 2,4-dinitrochlorobenzene and 6-aminoquinoline in an alcoholic solution in the presence of sodium acetate. Under these conditions the reaction is rather slow. A yield of 85% is acheived only after heating for more than 10 hours, the acetic acid that gradually forms being neutralized with soda.

The Methyl Betaine of 6-(2',4'-Dinitroanilino)-quinoline (II,b)

1.24 g of the methyl-p-toluene sulfonate of 6-(2',4'-dinitroanilino)-quinoline

is dissolved in 50 ml of 50% alcohol, and 1.2 g of 40% sodium hydroxide, diluted with 10 ml of 50% alcohol, is added drop by drop to the solution at 50-60°. When the very first drop of alkali is added, the color of the solution changes to dark red, and lustrous dark crystals soon begin to settle out. The precipitate is filtered out, washed with alcohol and water and dried in an exsiccator over sodium hydroxide. The yield is nearly quantitative. The finely crystalline product is dark gray with a golden lustre. Under the microscope it is seen to consist of hexagonal platelets (which are claret-colored in transmitted light). The compound does not melt when gradually heated to 300°, but when a capillary is placed in an instrument heated to 270-280°, decomposition is instantaneous. The product is insoluble in water, alcohol, and acetone, slightly soluble in nitrobenzene, and soluble with great difficulty in pyridine.

0.1054 g substance: 16.35 ml N_2 (24°, 753 mm)*.
Found %: N 17.27.
$C_{16}H_{12}O_4N_4$. Calculated%: N 17.28.

When acted upon by dilute mineral acids or acetic acid, the substance forms a yellow solution. After the excess acid has been neutralized, the addition of alkali (1-2 drops) causes an extremely sharp color transition to red. These properties of the betaine enable it to be analyzed by titration, the betaine itself serving as an indicator.

A weighed batch of the betaine is dissolved, with heating, in 20 ml of 0.1 N sulfuric acid and 25 ml of water. The excess acid is titrated back with 0.1 N NaOH. The solution is titrated while hot until the color changes from yellow-orange to orange-red.

0.3269 g substance: 10.05 ml 0.1 N H_2SO_4.
0.2717 g substance: 8.33 ml 0.1 N H_2SO_4.
Found %: betaine 99.70, 99.52.

6-Picrylaminoquinoline

The compound is synthesized with an almost quantitative yield by briefly heating picryl chloride with 6-aminoquinoline in alcoholic solution in the presence of soldium acetate. The orange crystals (from acetone) are soluble with difficulty in alcohol, but soluble fairly readily in nitrobenzene. When heated above 250° it gradually darkens and clinkers, fusing with decomposition above 270°; the decomposition temperature varies over a wide range in individual determinations.

0.1018 g substance: 17.55 ml N_2 (16.5°, 753 mm).
Found %: N 19.84.
$C_{15}H_9O_6N_5$. Calculated %: N 19.71.

The Methyl-p-toluene Sulfonate of 6-Picrylaminoquinoline (I,a)

This compound was synthesized by fusing 6-picrylaminoquinoline with methyl-p-toluenesulfonate at 140°. The yellow crystals (from methanol) with a m.p. of 257° are difficultly soluble in water. A precipitate of the betaine is thrown down when pyridine or sodium acetate is added to an aqueous solution.

0.2425 g substance: 0.1037 g $BaSO_4$ (Carius)
0.1579 g substance: 0.0673 g $BaSO_4$.
Found %: S 5.87, 5.85.
$C_{23}H_{19}O_9N_5S$. Calculated %: S 5.92.

The Methyl Betaine of 6-Picrylaminoquinoline (II,a)

An alcoholic solution of an alkali, taken in excess, or ammonia is added to a hot solution of the quaternary salt (I, a). The solution turns dark red, and a dark crystalline precipitate settles out. The product, washed with water and

*The volume of nitrogen was measured over a 33% solution of KOH.

methanol, is dried in vacuum over phosphorus anhydride. The yield is 95%. The brownish-purple crystals, are insoluble in benzene or chloroform, soluble with difficulty in acetone and pyridine, somewhat more easily in nitrobenzene, and very readily in dilute hydrochloric acid. The substance does not melt when gradually heated up to 330°; but if a capillary is placed in an instrument heated to 315°, rapid decomposition sets in.

0.1042 g substance: 17.75 ml N_2 (15.5°, 727 mm).
Found %: N 19.02.
$C_{16}H_{11}O_6N_5$. Calculated %: N 18.97.

The Methyl-p-toluene Sulfonate of 6-(p-Toluene Sulfamino)-quinoline (I, c)

The initial 6-(p-toluene sulfamino)-quinoline [6] was prepared by the action of p-toluene sulfochloride on 6-aminoquinoline in a solution of pyridinic bases (115-130° fraction). Yield: 94%. M.p. 196-197°.

A mixture of 4 g of powdered 6-(p-toluene sulfamino)-quinoline and 2.5 g of methyl p-toluene sulfonate is heated to 140° over an oil bath for 1½ hours. The melt is ground to powder and the unreacted initial substances are extracted with boiling benzene. The yield is 6.0 g (92%). The yellowish-white lamellar crystals (from alcohol) are soluble with difficulty in water. M.p. 271-272°.

0.1582 g substance: 0.1510 g $BaSO_4$ (Carius)
0.1738 g substance: 0.1642 g $BaSO_4$.
Found %: S 13.11, 12.98.
$C_{24}H_{24}O_5N_2S_2$. Calculated %: S 13.23.

The Methyl Betaine of 6-(p-Toluene Sulfamino)-quinoline (II,c).

2.42 g of the methyl-p-toluene sulfonate of 6-(p-toluene sulfamino)-quinoline is dissolved in 300 ml of boiling water. The solution is cooled to 75°, and 4 ml of 15% ammonia is added to it; this turns the solution an intense orange-yellow. Upon cooling, thin orange needles* settle out; they are filtered out, washed with dilute ammonia and with water, and dried to constant weight in an exsiccator over sodium hydroxide. Yield: 1.60 g (92%). Crystallization from 75% alcohol. The crystals lose two molecules of water, turning into an anhydrous red betaine, when allowed to stand for a short time (overnight) in an vacuum exsiccator over phosphorous anhydride or when heated (rapidly at 70-80° in a vacuum). The orange crystals are, therefore, the monohydrate of a base or, more likely,** the dihydrate of a betaine.

This loss of water is likewise observed when it is allowed to stand in an exsiccator over calcium chloride for a long time.

0.4958 g substance: loss in weight 0.0509 g (in vacuum over P_2O_5)
0.4520 g substance: loss in weight 0.0465 g.
0.1752 g substance: 0.1175 g $BaSO_4$ (Carius).
0.1528 g substance: 0.1012 g $BaSO_4$.
Found %: H_2O 10.27, 10.29; S 9.21, 9.10.
$C_{17}H_{16}O_2N_2S \cdot 2H_2O$. Calculated %: H_2O 10.34; S 9.20.

The red betaine crystals are insoluble in ether, benzene, or dioxane, almost insoluble in absolute alcohol or acetone, and slightly soluble in nitrobenzene.

The action of dilute hydrochloric acid gives rise to a difficultly soluble

*Orange crystals are also formed when soda or an alkali is used for the reaction.

**This hypothesis is based upon the deep color of the substance and upon the observation that both molecules of water are eliminated with equal ease.

hydrochloride; the betaine dissolves readily in dilute acetic acid. When allowed to stand over a dilute alkali solution it adds two molecules of water. Reaction with p-toluene sulfonic acid in an aqueous alcoholic solution results in the formation of the initial methyl-p-toluene sulfonate of 6-p-toluene sulfaminoquinoline.

The melting point of the product depends upon the initial temperature and the rate of heating; with very slow heating (from 230°) fusion takes place at 238.5-239.5° (with decomposition).

3.941 mg substance: 0.306 ml N_2 (13.0°, 731.5 mm).
3.686 mg substance: 0.289 ml N_2 (11.5°, 735 mm).
0.1568 g substance: 0.1160 g $BaSO_4$ (Carius).
0.1764 g substance: 0.1308 g $BaSO_4$.
0.1827 g substance: 0.1355 g $BaSO_4$.
Found %: N 8.90, 9.10; S 10.16, 10.23; 10.19.
$C_{17}H_{16}O_2N_2S$. Calculated %: N 8.97; S 10.26.

SUMMARY

1. The betaine azeniates of the quinoline series, with structures II,a, II,b, and II,c have been synthesized.

2. The betaine azeniates of structures II,a, and II,b are easily formed by reacting slightly alkaline agents with the corresponding salts of quinoline (I,a, I,b).

3. When reacted with ammonia, the quaternary salt of structure I,b forms a monohydrate of a base (a dihydrate of the betaine), which loses water readily, being converted into the betaine.

4. These betaine azeniates of the quinoline series are formed more readily than the corresponding compounds of the benzene series (IV, a - c).

5. The experimental data obtained indicate that in the quaternary ammonium salts of the type studied, an increase in the electrophilic nature of the radicals attached to the NH group facilitates the detaching of hydrogen from the NH group, resulting in the formation of betaine azeniates.

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Received June 27, 1948.

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*See CB translation p. a683 ff.

THE REACTION OF ORTHO AND PARA DITOLYLMERCURY WITH ORGANIC ACIDS*

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Comparatively little work has been done on the reactions of tolyl derivatives of mercury, and their reaction with organic acids has been investigated only in the instance of p-ditolylmercury and acetic acid [1].

We have explored the reaction of p-ditolylmercury with the following acids: 1) formic, 2) valeric, 3) benzoic, 5) salicylic, and 6) oxalic acids, and the reaction of o-ditolylmercury with these acids: 1) formic, 2) acetic, 3) isovaleric, 4) lactic, 5) salicylic, and 6) oxalic acids. In all cases toluene is evolved and compounds of the RHgOCOR' type are formed, in accordance with the equation:

$$R_2Hg + HOCOR' = RHgOCOR' + RH,$$

where R' is the organic acid radical, and R is the tolyl radical (ortho or para).

Acyl derivatives are produced by the action of p-ditolylmercury as well as o-ditolylmercury, but the rate of their formation differs. Ortho ditolylmercury is more reactive. Formic acid, for instance, reacts with o-ditolylmercury at room temperature, whereas heating to 100° for 2 hours is required for the formation of p-tolylmercury formate. Only formic and acetic acids react with o-ditolylmercury at room temperature, the other acids requiring heating to 100° for 1 hour.

Only formic acid reacts with p-ditolylmercury at 100°, the other acids requiring heating to 130° and even 150°. The acyl derivatives of p-ditolylmercury have higher melting points than the corresponding compounds of o-ditolylmercury. All the acyl compounds that are derivatives of p-ditolylmercury are insoluble in organic solvents, with the exception of p-tolylmercury formate. On the other hand, the compounds synthesized from o-ditolylmercury are all readily soluble in organic solvents, except for o-tolylmercury oxalate. All the acyl derivatives of para and ortho ditolylmercury are crystalline substances with sharply defined melting points, with the exception of p-tolylmercury lactate, which is an infusible compound.

EXPERIMENTAL

All experiments were carried out in sealed glass ampoules, which were either heated over a water bath or in an oil thermostat with automatic temperature regulation. After heating was complete, the contents of the ampoules were treated with water and heated. Whenever necessary, the synthesized substance was recrystallized. Analysis for mercury was performed in the usual manner, [2].

1. Para ditolylmercury and formic acid. 0.2 g of p-ditolylmercury and 1 ml of formic acid are heated at 100° for 2 hours. After the reaction mixture has been treated with water, a white precipitate is formed. Recrystallization from a solution of formic acid yields 0.11 g (62.5% of the theoretical) of a white powder insoluble in ether, poorly soluble in alcohol, and readily soluble in acetone or benzene when heated, with a m.p. of 220-222°.

* Candidate dissertation (1948).

0.05 g substance: 2.967 ml 0.1 N NH_4CNS.
Found %: Hg 59.34.
$CH_3C_6H_4HgOCOH$. Calculated %: Hg 59.59.

The substance is p-tolylmercury formate.

2. Ortho ditolylmercury and formic acid. 1 ml of formic acid is combined with 0.2 g of o-ditolylmercury. The reaction is effected at room temperature, being completed in 15-20 hours, with all the o-ditolylmercury dissolving. Treatment of the solution with water causes a grayish-white crystalline precipitate to settle out, which is soluble in the cold in ether, alcohol, acetone, and benzene and insoluble in hot water; it has a m.p. of 88-89°, and the yield is 0.11 g (62.5% of the theoretical).

0.05 g substance: 3.00 ml 0.1 N NH_4CNS.
Found %: Hg 60.00.
$CH_3C_6H_4HgOCOH$. Calculated %: Hg 59.59.

The substance is o-tolylmercury formate.

3. Ortho ditolylmercury and acetic acid. 1 ml of acetic acid is used per 0.2 g of o-ditolylmercury. The reaction takes place at room temperature and is concluded within 42 hours, all of the o-ditolylmercury entering into solution. Treatment of the solution with water results in the formation of a white crystalline precipitate, soluble in the cold in ether, alcohol, acetone, and benzene, with a m.p. of 92°, its yield is 0.11 g (60.1% of the theoretical).

0.05 g substance: 2.90 ml 0.1 N NH_4CNS.
Found %: Hg 58.00.
$CH_3C_6H_4HgOCOCH_3$. Calculated %: Hg 57.22.

The substance is o-tolylmercury acetate.

4. Para ditolylmercury and isovaleric acid. 0.2 g of p-ditolylmercury and 1 ml of isovaleric acid are heated to 150° for 3 hours.

The reaction mixture is treated with water and heated. 0.045 g (22% of the theoretical) of a light yellow powder, with a m.p. of 160-162° is secured from the aqueous solution.

0.03 g substance: 1.520 ml 0.1 N NH_4CNS
Found %: Hg 50.70.
$CH_3C_6H_4HgOCOCH_2CH(CH_3)_2$. Calculated %: Hg 51.09.

The substance is p-tolylmercury isovalerate.

5. Ortho ditolylmercury and isovaleric acid. 0.2 g of o-ditolylmercury and 1 ml of isovaleric acid are heated to 100° for 1 hour. The solution is treated with water, causing 2 layers to form. Evaporation of the lower layer causes a white crystalline precipitate to settle out. The substance is readily soluble in ether, alcohol, acetone, and benzene; its m.p. is 52°, and its yield 0.06 g (30% of the theoretical).

0.05 g substance: 2.535 ml 0.1 N NH_4CNS.
Found %: Hg 50.70.
$CH_3C_6H_4HgOCOCH_2CH(CH_3)_2$. Calculated %: Hg 51.09.

The substance is o-tolylmercury isovalerate.

6. Para ditolylmercury and hydroxypropionic acid. 0.3 g of p-ditolylmercury and 1 ml of hydroxypropionic acid are heated to 130° for 6 hours. After the reaction mixture is treated twice with hot water, a light-brown product is left, which is insoluble in organic solvents and infusible up to 250°.

0.05 g substance: 2.60 ml 0.1 N NH_4CNS.
Found %: Hg 52.00.
$CH_3C_6H_4HgOCOCH(OH)CH_3$. Calculated %: Hg 52.71.

The substance is p-tolylmercury lactate.

7. Ortho ditolylmercury and hydroxypropionic acid. 0.2 g of o-ditolylmercury and 1 ml of hydroxypropionic acid are heated to 100° for 1 hour. The reaction mixture consists of 2 liquid layers. Treatment of the mixture with water causes a white crystalline precipitate, with a m.p. of 124°, soluble in benzene and acetone, to settle out of the aqueous solution.

0.05 g substance: 2.633 ml 0.1 N NH_4CNS.
Found %: Hg 52.66.
$CH_3C_6H_4HgOCOCH(OH)CH_3$. Calculated %: Hg 52.71.

The substance is o-tolylmercury lactate.

8. Para ditolylmercury and oxalic acid. 0.3 g of p-ditolylmercury and 0.3 g of oxalic acid are heated to 130° for 3 hours in the presence of one drop of water. The product is carefully treated with hot water to eliminate the unreacted oxalic acid. 0.09 g (30% of the theoretical) of a white crystalline precipitate is left, insoluble in organic solvents, with a m.p. of 214-216°.

0.05 g substance: 2.65 ml 0.1 N NH_4CNS.
Found %: Hg 53.00.
$CH_3C_6H_4HgOCOCOOH$. Calculated %: Hg 52.71.

The substance is p-tolylmercury oxalate.

9. Ortho ditolylmercury and oxalic acid. 0.2 g of o-ditolylmercury and 0.1 g of oxalic acid are heated to 100° for 1 hour in the presence of one drop of water. The reaction mass is carefully treated with water and heated with a reflux condenser to effect complete elimination of the unreacted oxalic acid. There remains 0.04 g (20% of the theoretical) of a white crystalline precipitate, insoluble in ether, alcohol, and benzene, with a m.p. of 161-163°.

0.03 g substance: 1.58 ml 0.1 N NH_4CNS.
Found %: Hg 52.66.
$CH_3C_6H_4HgOCOCOOH$. Calculated %: Hg 52.71.

The substance is o-tolylmercury oxalate.

10. Para ditolylmercury and benzoic acid. 0.16 g of p-ditolylmercury and 0.16 g of benzoic acid are heated to 150° for 6 hours. The reaction mixture is treated with water until the unreacted benzoic acid is eliminated. There remains 0.05 g (30% of the theoretical) of a white crystalline precipitate with a m.p. of 213-215°, insoluble in ether, alcohol, and benzene.

0.03 g substance: 1.46 ml 0.1 N NH_4CNS.
Found %: Hg 48.66.
$CH_3C_6H_4HgOCOC_6H_5$. Calculated %: Hg 48.62.

The substance is p-tolylmercury benzoate.

11. Para ditolylmercury and ortho hydroxybenzoic acid. 0.3 g of p-ditolylmercury and 0.3 g of o-hydroxybenzoic acid are heated to 130° for 6 hours. The reaction mixture is treated with water to eliminate the unreacted o-hydroxybenzoic acid completely. There remains 0.14 g (41% of the theoretical) of a light-pink crystalline precipitate, with a m.p. of 190°, which is insoluble in ether, alcohol, or benzene.

0.05 g substance: 2.335 ml 0.1 N NH_4CNS.
Found %: Hg 46.70.
$CH_3C_6H_4HgOCOC_6H_4(OH)$. Calculated %: Hg 46.80.

The substance is p-tolylmercury salicylate.

12. Para ditolylmercury and o-hydroxybenzoic acid. 0.2 g of o-ditolylmercury and 0.08 g of o-hydroxybenzoic acid are heated to 100° for 1 hour. The reaction mixture is treated with hot water until all the unreacted o-hydroxybenzoic acid is eliminated. There remains a white crystalline precipitate with a m.p. of 107-108° insoluble in ether, but readily soluble in acetone and benzene.

0.05 g substance: 2.335 ml 0.1 N NH_4CNS.
Found %: Hg 46.70.
$CH_3C_6H_4HgOCOC_6H_4(OH)$. Calculated %: Hg 46.80.

The substance is o-tolylmercury salicylate.

SUMMARY

1. The reaction of ortho and para ditolylmercury with 8 organic acids has been investigated, and it has been established that in these reactions acyl derivatives of ditolylmercury of the RHgOCOR type are formed, and that toluene is evolved.

2. It has been established that o-ditolylmercury is more reactive than p-ditolylmercury.

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Received July 1, 1948.

OXIDATION OF OXIMES OF THE POLYMETHYLENE SERIES

VI. THE BEHAVIOR OF THE OXIME OF CYCLOHEXANONE WITH OXIDANTS

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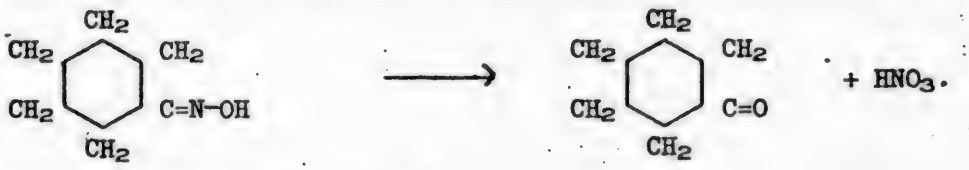
In our first report [1], one of the present authors established that cyclohexanone was formed from cyclohexylamine in catalytic oxidation by oxygen in the presence of copper.

To establish the reaction mechanism of the oxidation of amines of the polymethylene series, it is desirable to trace the behavior of other nitrogen compounds related to the amines, which may be formed as intermediate products during oxidation. We considered a few oximes of the polymethylene series, whose behavior with oxidizing agents did not constitute the subject of special investigation. We took cyclohexanone oxime, which one of the present authors repeatedly produced during a conversion to cyclohexylamine.

The probable course of the process of oxidizing the cyclohexanone oxime is as follows:



EXPERIMENTAL

To prepare the oxime, we took cyclohexanone, with a b.p. of 154-155°. The cyclohexanone oxime was prepared as follows, by the method described by Hentschel and Wislicenus [1]: the ketone was dissolved in alcohol, and hydroxyl hydrochloride was added; the mixture was gradually mixed with a saturated soda solution and agitated. When it was evaporated over a water bath, the aqueous solution had a supernatant oil with a disagreeable odor, which hardened into a solid crust upon cooling. The oxime was recrystallized from alcohol. A total of 43 g of the cyclohexanone oxime was recovered. The yield was 60-65% of the theoretical.

Oxidation of the cyclohexanone oxime by hydrogen peroxide. 5 g of the cyclohexanone oxime, dissolved in petroleum ether, was placed in a 250-ml round-bottomed flask fitted with a reflux condenser. Perhydrol was added in small batches. A total of 45 ml of hydrogen peroxide was used. The reaction mass was heated over a water bath for 32 hours. The liquid in the reaction flask separated into two layers. The upper layer was yellow. This colored layer was removed in a separating funnel. The petroleum ether was driven off. There remained a mobile yellow oil with the pepermint odor of cyclohexanone. 1.1 g of cyclohexanone was recovered. The yield of the ketone was 22% of the theoretical. We synthesized the ketone's semicarbazone, which was recrystallized from boiling alcohol, settling out as tiny crystals with a m.p. of 165-166°. The aqueous solution left after the cyclohexanone had been separated was tested for the presence of nitrogen compounds. Nitric acid

was found.

Oxidation of cyclohexanone oxime with a solution of potassium permanganate. 5 g of the oxime, dissolved in 75 ml of petroleum ether, were used for oxidation. 25 g of the oxidizing agent was used. The mixture was heated over a water bath for 24 hours. Then the top layer was removed in a separating funnel, and the petroleum ether was driven off; what was left was 1 g of a yellow oil with the odor of cyclohexanone. The yield was 20% of the theoretical, based on the amount of the oxime used. 0.55 g of the unreacted oxime was recovered. Nitric acid was found in the aqueous solution after the manganese dioxide had been filtered out.

Oxidation of cyclohexanone oxime by chromic anhydride. 5 g of cyclohexanone oxime, dissolved in 75 ml of petroleum ether, was used. 14 g of chromic anhydride, in 25 ml of distilled water, was used. The reaction mixture was heated for 24 hours over a water bath. 0.9 g of cyclohexanone was produced. We recovered 0.59 g of unreacted oxime. Nitric acid was found.

SUMMARY

Oxidation of cyclohexanone by hydrogen peroxide, potassium permanganate, and chromic anhydride results in the formation of cyclohexanone and nitric acid.

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Received July 1, 1948.

THE OXIDATION OF ALIPHATIC AMINES

VII. BEHAVIOR OF DIETHYLAMINO-4 AMINOPENTANE WITH OXIDANTS

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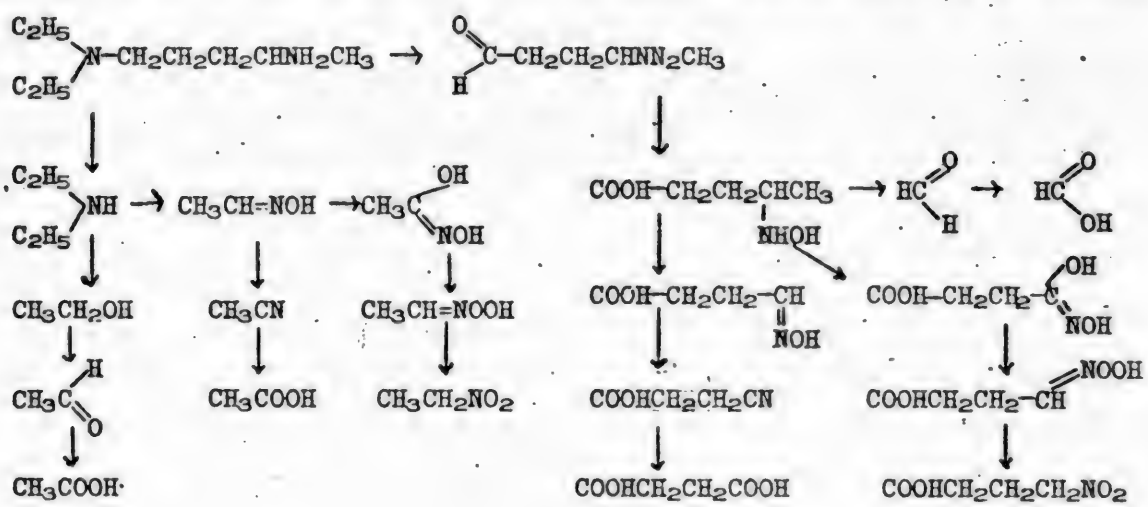
In our research on the oxidation of amines we have noted several courses taken by the oxidation process for primary, secondary, and tertiary amines of the aliphatic series. Of the primary amines, we have explored n-butylamine; of the secondary amines, diethylamine, and dibutylamine; and of the tertiary amines, 1-diethylaminobutanone and diethylaminoethanol.

We undertook the investigation of diethylamino-4-aminopentane (I). No special research has been done on the behavior of this amine with oxidizing agents. The probable course of the oxidation of diethylamino-4-aminopentane is as follows:



EXPERIMENTAL

We used ready diethylamino-4-aminopentane, in the form of a colorless liquid with the odor of piperidine and a b.p. of 197-200° at 760 mm. It is readily soluble in water, alcohol, and ether, and fumes in air, attracting carbon dioxide.

Oxidation by hydrogen peroxide. 10 g of diethylamino-4-aminopentane was placed in a 100-ml round-bottomed flask, connected to a reflux condenser and a dropping funnel, and 30% perhydrol was added in small batches. As the hydrogen peroxide was added, the temperature quickly rose to 60° without external heating. The mixture began to boil. The reaction liquid was heated for 64 hours over a water bath. 50 ml of hydrogen peroxide was consumed. It should be noted that oxidation is violent at the start, but the odor of the amine does not disappear for several days. The entire mixture was distilled with a dephlegmator. This yielded the following fractions:

1 – up to 80°; 1.6 g. 2 – 80-120°: 31.2 g; and a residue of 15 g.

Part of the fraction boiling up to 80° was heated with a few iodine crystals and a small amount of an aqueous solution of soda to detect ethyl alcohol, by the Lieben method. Crystals of iodoform settled out upon standing. Some of the 80-120° fraction, with an acid litmus reaction, was neutralized with an aqueous solution of sodium hydroxide. Evaporation yielded a small quantity of crystals.

The addition of concentrated sulfuric acid to the crystalline product yielded free acetic acid. Part of this same fraction was evaporated to dryness with potassium hydroxide, and a small quantity of arsenic trioxide was added. This gave rise to the disagreeable odor of cacodyl, indicating the presence of acetic acid in the oxidation products.

The 80-120° fraction is readily reduced by Fehling's solution, producing a red precipitate of cuprous oxide. Ammoniacal silver nitrate is reduced, forming a silver mirror. Some of the fraction was heated with 2 ml of fresh milk, 7 ml of hydrochloric acid, and 0.5 ml of a 5% solution of ferric chloride. The characteristic purple color of formaldehyde quickly made its appearance.

Treating a small quantity of the fraction boiling above 120° with aqueous ferric chloride turned the solution an intense red. When the solution was treated with copper sulfate, it turned bright green, and a green precipitate settled out a few minutes later. These two color reactions indicate the presence of hydroxamic acids.

Some of the fraction was treated with 4 ml of 1N hydrochloric acid and then evaporated. The crystals produced were repeatedly treated with absolute ethyl alcohol to remove any salt of the initial amine possibly present. After the ethyl alcohol had been driven off in vacuum, the crystals that remained already exhibited the odor of the initial amine when decomposed with an aqueous solution of an alkali. The crystals, which were insoluble in absolute alcohol, liberated ammonia when treated with the aqueous alkali solution. The remainder of the fraction was evaporated, yielding a certain quantity of crystals, which fused at 182° after recrystallization from hot water and careful drying in vacuum. A test sample mixed with succinic acid exhibited no depression of the melting point. The crystals exhibited a marked pyrrole reaction.

Oxidation by potassium permanganate. 10 g of diethylamino-4-aminopentane was placed in a 100-ml round-bottomed flask equipped with a reflux condenser and a dropping funnel, and 40 ml of aqueous potassium permanganate, containing 18 g of the oxidizing agent, was added gradually. The oxidizing reaction was slow. The reaction mixture was heated for 64 hours until the amine odor had vanished.

The manganese dioxide was filtered out and washed with a small quantity of hot water. The solution was fractionated after this filtration. The following fractions were recovered: 1 – up to 80°: 1.5 g; 2 – 80-120°: 30.7 g; and 12.8 g of residue. Ethyl alcohol, acetic acid, hydroxamic acids, formaldehyde, succinic acid, and ammonia were identified among the products of oxidation.

Oxidation by chromic anhydride. 10 g of diethylamino-4-aminopentane was placed in a 100-ml round-bottomed flask fitted with a reflux condenser, and 20 g of chromic anhydride dissolved in 40 ml of distilled water was gradually added. The oxidation reaction was slow. The black mass that was formed was filtered out. The whole reaction mass was fractionated, yielding the following fractions: 1 – up to 80°: 1.3 g; 2 – 80-120°: 32 g. Ethyl alcohol, acetic acid, hydroxamic acids, formaldehyde, succinic acid, and ammonia were identified among the products of oxidation.

SUMMARY

In the oxidation of diethylamino-4-aminopentane by hydrogen peroxide, potassium permanganate, and chromic anhydride, ethyl alcohol, acetic acid, hydroxamic acids, formaldehyde, succinic acid, and ammonia were identified in the oxidation products.

Received July 1, 1948.

THE OXIDATION OF ALIPHATIC AMINES

VIII. BEHAVIOR OF N-BUTYLAMINE AND DIBUTYLAMINE WITH OXIDANTS

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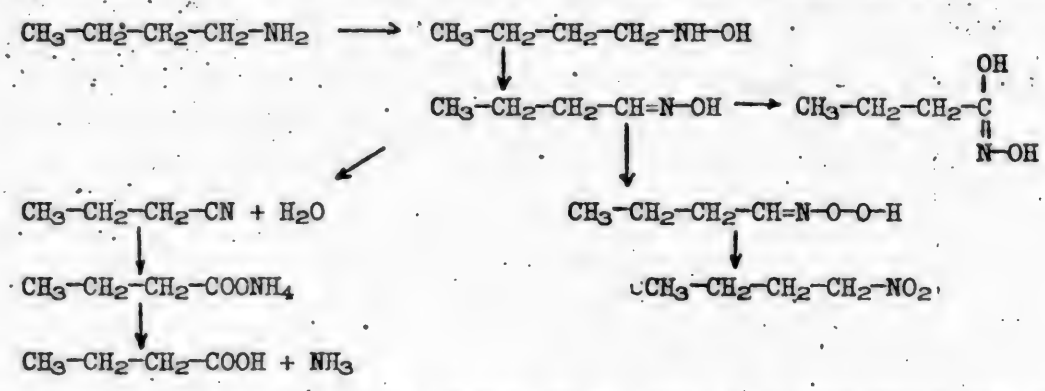
In our former researches [1] on the oxidation of diethylamine, 1-diethylaminobutanone, and diethylaminoethanol we pointed out several paths taken by the oxidation process for these amines of the aliphatic series.

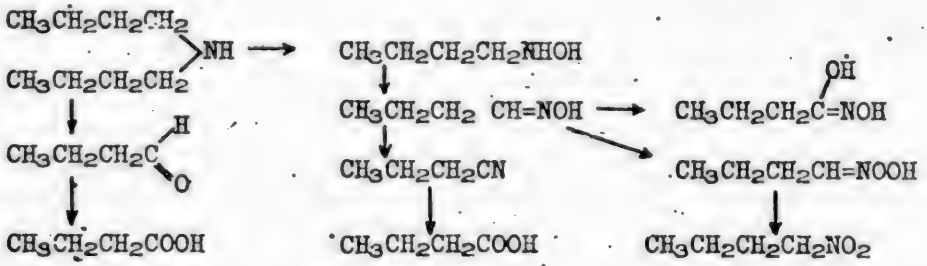
In 1903, Bamberger and Seligman [2], when oxidizing tert-butylamine, found the corresponding hydroxylamine derivatives, which were converted into nitro and nitro compounds upon further oxidation. Goldschmidt and Beuschel [3] oxidized tert-butylamine with Caro's acid and discovered that the tert-amine was proof against this oxidizing agent.

To purify primary amines of traces of secondary amines, Begai and Wallis [4] oxidized butylamine, amylamine, and benzylamine with potassium permanganate in the presence of sulfuric acid, and established the fact that these amines oxidize readily. Analysis of the oxidation products was not the object of their research.

In the present report we describe the results of oxidizing n-butylamine and dibutylamine. The course of the oxidation of n-butylamine is probably as follows:



The oxidation of dibutylamine is similar to that of n-butylamine and probably follows the course:



EXPERIMENTAL

In our research we used ready n-butylamine, with a b.p. of 76-77°; d_4^{20} 0.7422. In our experiments we used the freshly distilled amine.

Oxidation of n-butylamine by hydrogen peroxide. 10 g of n-butylamine was placed in a 100-ml round-bottomed flask fitted with a reflux condenser and a dropping funnel, and perhydrol was added in small batches. The perhydrol consumed totalled 50 ml. The reaction liquid was heated over a water bath for 48 hours, because of the slowness with which the amine oxidized; as a result of the prolonged heating, the odor of n-butylamine vanished. After oxidation the solution was pale yellow and had a disagreeable rancid smell. The mixture was then fractionated, yielding the following fractions: 1st – up to 105°: 44.5 g; 2nd – 105-165°: 4.5 g; and 3.84 g of residue.

No oxidation products were found in the first fraction. The 105-165° fraction with the disagreeable odor of rancid oil was refractionated from a small Würtz flask; the following fractions were recovered: 1st – 105-160°: 1.12 g; 2nd – 160-165°: 2.82 g (with a disagreeable odor of rancid oil); d_4^{20} 0.975.

Treatment of a small amount of the second fraction with a hot, transparent solution of potassium chloride caused a white precipitate, characteristic of potassium n-butyrate, to settle out. The remainder of the fraction was treated with ethyl alcohol in the presence of a small quantity of sulfuric acid. After purification, we recovered 11.74 g of a reaction product with a b.p. of 121°, with the pleasant banana odor typical of ethyl butyrate. These data testify to the presence of n-butyric acid in this fraction.

Part of the fraction that boils over 165° was treated with aqueous ferric chloride. This turns the solution an intense red. When a small quantity of this fraction was treated with aqueous copper sulfate, the solution turned bright green, and a green precipitate settled out after a few minutes had passed. These two typical color reactions testify to the presence of butyrohydroxamic acid. The rest of the fraction was treated with 4 ml of n-hydrochloric acid and evaporated. The crystals produced were treated repeatedly with absolute ethyl alcohol to remove any salt of the initial amine that might be present. After the alcohol was removed, there remained a small quantity of crystals, whose decomposition with an aqueous alkali solution produced the characteristic odor of the initial amine.

Treatment of the remaining crystals, which were insoluble in absolute alcohol, with an aqueous solution of sodium hydroxide produced the sharp odor of ammonia.

Oxidation of dibutylamine by hydrogen peroxide. 10 g of dibutylamine was placed in a 100-ml round-bottomed flask, fitted with a reflux condenser and a dropping funnel, and perhydrol was added in small batches. 50 ml of perhydrol was used. The reaction mass was heated over a water bath for 64 hours, because of an even greater slowness of oxidation that we observed in the case of n-butylamine. After 64 hours had elapsed the odor of the amine vanished, and a rancid, disagreeable odor took its place. The solution was colored pale yellow. The mixture was then fractionated, yielding the following fractions: 1st – up to 105°: 40 g; 2nd – 105-165°: 3.2 g; residue: 5.5 g.

The 105-165° fraction, with the unpleasant odor of rancid oil, was fractionated in a small Würtz flask, the following fractions being recovered: 1st – 105-165°: 0.82 g; 2nd – 160-165°: 1.8 g.

N-butyric acid and butyrohydroxamic acid were found in the oxidation products.

The rest of the fraction was treated with 6 ml of 1 N sulfuric acid and then evaporated over a water bath to minimum volume. The crystals recovered were treated

repeatedly with absolute ethyl alcohol to remove any salt of the initial amine that might be present. After the absolute alcohol had been driven off in vacuum, decomposition of the remaining crystals with an aqueous alkali solution produced the marked odor of the initial amine. The crystals, which were insoluble in absolute alcohol, liberated ammonia when treated with an aqueous solution of alkali.

In fractionating the reaction mixture into the fractions boiling below 105° and from 105-165°, a small amount of an oil product with an unpleasant smell was found on the surface of the liquid.

Oxidation of n-butylamine by chromic anhydride. 10 g of the amine was placed in a round-bottomed flask fitted with a reflux condenser and a dropping funnel, and 20 g of chromic anhydride dissolved in 40 ml of distilled water was gradually added. The oxidation reaction was a quiet one. Heating over a water bath was continued for 48 hours until the odor of the amine was no longer present. A small amount of a black mass was formed; this was filtered out. The product, which had an unpleasant rancid odor, was fractionated. The following fractions were recovered: 1st – up to 105°: 43 g; 2nd – 105-165°: 4.1 g; and a residue of 3.62 g.

No oxidation products were found in the first fraction. The 105-165° fraction, with the odor of rancid oil, was refractionated from a small Würtz flask. The following fractions were recovered: 1st – 105-160°: 1 g; 2nd – 160-165°: 2.62 g; d_4^{20} 0.973.

No oxidation products were found in the 105-160° fraction. The 160-165° fraction contained n-butyric acid, butyrohydroxamic acid, and ammonia.

Oxidation of dibutylamine by chromic anhydride. 10 g of the amine was placed in a round-bottomed flask fitted with a reflux condenser and a dropping funnel, and 20 g of chromic anhydride dissolved in 40 ml of distilled water was gradually added.

The oxidation reaction was slow. Heating over a water bath continued for 64 hours. The black mass that formed was filtered out. All the reaction mass, with an unpleasant rancid odor, was fractionated, yielding the following fractions: 1st – up to 105°: 41 g; 2nd – 105-165°: 3.75 g; and a residue of 2.4 g.

No oxidation products were found in the first fraction. The 105-165° fraction was refractionated, yielding the following fractions: 1st – 105-160°: 0.8 g; 2nd – 160-165°: 1.7 g.

N-butyric acid, butyrohydroxamic acid, and ammonia were found in the oxidation products.

No oily layer, such as had been seen during oxidation by hydrogen peroxide, was observed during fractionation of the reaction product after oxidation by chromic anhydride.

Oxidation of n-butylamine by potassium permanganate. The n-butylamine was placed in a flask fitted with a reflux condenser and a dropping funnel, and 40 ml of an aqueous solution of potassium permanganate, containing 18 g of the oxidizing agent, was gradually added. The oxidation of this amine is fairly slow. The reaction mixture was heated over a water bath for 48 hours until the odor of the amine had vanished. The manganese dioxide was filtered out of the solution and washed several times with small quantities of hot water. After filtering, the solution was fractionated, the following fractions being recovered: 1st – up to 105°: 44.59 g; 2nd – 105-165°: 3.89 g; and a residue of 3.8 g.

No oxidation products were found in the first fraction. The 105-165° fraction, with the odor of rancid oil, was refractionated, yielding the following fractions: 1st – 105-160°: 1.1 g; 2nd – 160-165°: 2.2 g; d_4^{20} 0.982.

N-butyric acid, butyrohydroxamic acid, and ammonia were found among the oxidation products.

Oxidation of dibutylamine by potassium permanganate. 10 g of dibutylamine was placed in a flask fitted with a reflux condenser and a dropping funnel, and 40 ml of an aqueous solution of potassium permanganate, containing 18 g of the oxidizing agent, was added gradually. The reaction mixture was heated over a water bath for 64 hours. The manganese dioxide was filtered out and then washed with a small quantity of hot water. After filtration, the solution was fractionated, yielding the following fractions: 1st – up to 105°: 42.1 g; 2nd – 105-165°: 3.2 g; and a residue of 2.7 g.

No oxidation products were found in the first fraction. The 105-165° fraction with the odor of rancid oil, was refractionated, yielding the following fractions: 1st – up to 105°: 0.9 g; 2nd – 105-165°: 1.8 g.

N-butyric acid, butyrohydroxamic acid, and ammonia were found in the oxidation products.

SUMMARY

1. N-butyric acid, butyrohydroxamic acid, and ammonia were found in the products of the oxidation of n-butylamine by hydrogen peroxide, chromic anhydride, and potassium permanganate.

N-butyric acid, butyrohydroxamic acid, and ammonia were found in the products of the oxidation of dibutylamine by hydrogen peroxide, chromic anhydride, and potassium permanganate.

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[1] V.S.Smirnov and E.A.Shklyaruk, J. Gen. Chem., 16, 1443 (1946); 16, 1687 (1946); 16, 1693 (1946).

[2] Bamberger and Seligman, Ber., 36, 701 (1903).

[3] Ber., 36, 685 (1903).

[4] Lieb. Ann., 261, 250 (1906).

Received July 1, 1948.

THE ACTION OF PHOSPHORUS PENTACHLORIDE AND PENTABROMIDE UPON ANTHRACENE AND ITS DERIVATIVES

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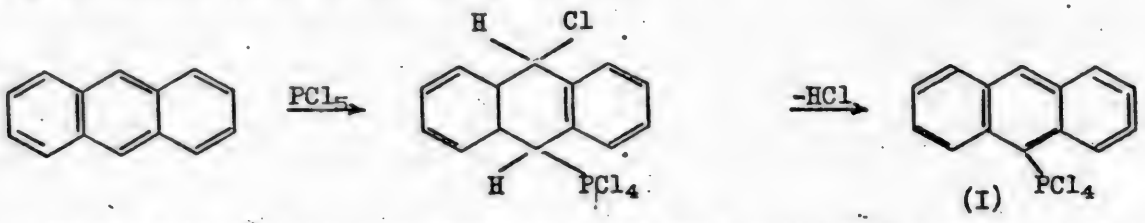
In many of its chemical transformations, anthracene behaves like an unsaturated compound, containing one or more multiple carbon-carbon bonds. Thus, for example, anthracene adds halogens, alkali metals, and maleic anhydride. It might be expected that, like unsaturated hydrocarbons, anthracene and its derivatives would not prove to be inert toward the phosphorus pentahalides.

In the light of the behavior of ethylene [1,2,3], acetylene [1,4], and diene [2,5] compounds with phosphorus pentachloride, adding a chlorine atom and PCl_4 at the multiple bond, it seemed most likely that the reaction of anthracene with phosphorous pentachloride would result in the formation of 9-anthryltetrachlorophosphine (I), in accordance with the following diagram:

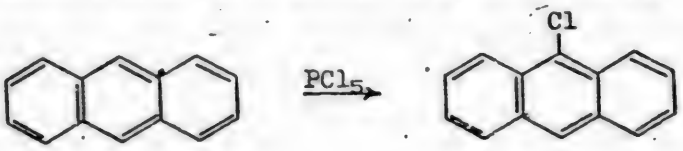


(I)

Study of the reaction of anthracene with PCl_5 indicated, however, that the end product of the reaction in a benzene medium was 9-chloroanthracene instead of the phosphorus-organic compound.

When equimolecular quantities of anthracene and PCl_5 are reacted together at room temperature for 80 hours, we get 45% of the theoretical yield of 9-chloroanthracene. At a higher temperature (with the reaction mixture heated over a water bath), the reaction rate is increased considerably, 19% of the chloroanthracene being obtained within 5 minutes and a 69% yield of 9-chloroanthracene being formed within an hour.

Prolonging the reaction to 2 hours merely results in an extremely small yield of chloroanthracene, with about 20% of the hydrocarbon remaining unchanged.



(II)

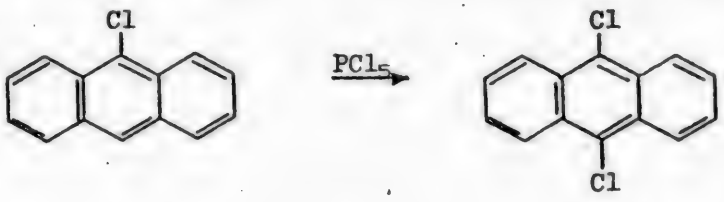
When two equivalents of phosphorus pentachloride are used, we get 9,10-dichloroanthracene, in addition to the monochloro derivative. 59% of the theoretical yield of 9-chloroanthracene and 12.7% of 9,10-dichloroanthracene were recovered in an experiment performed at room temperature, lasting 160 hours.

The reaction between anthracene and PCl_5 is a simple method of preparing 9-chloroanthracene.

According to Perkin [6], 9-chloroanthracene is produced by the action of chlorine upon a solution of anthracene in hydrogen sulfide at 0°; anthracene dihydrochloride first separates out, losing hydrogen chloride at room temperature. The author does not state the yield. 9-Chloroanthracene is likewise produced by the action of chloroacetamide upon anthracene, but the yield is poor [7]. Clark [8] synthesized 9-chloroanthracene by the reaction of tertiary butyl hypochlorite upon anthracene, but he says nothing about this method of chlorinating anthracene, stating merely that a considerable yield of 9-chloroanthracene is recovered.

The meso-monohalogen derivatives of anthracene react like anthracene with phosphorus pentachloride; the end products of the reaction are meso-dihalogen derivatives of anthracene.

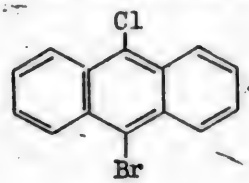
The above-mentioned experiments on the action of an excess of phosphorus pentachloride upon anthracene, in which 9,10-dichloranthracene was recovered in addition to 9-chloroanthracene, should have led us to conclude that the monochloro-derivative is formed at a higher rate than the dihalogen derivative. Actual tests of the reaction of 9-chloroanthracene with an excess of phosphorus pentachloride showed that chloroanthracene reacts more slowly than anthracene with PCl_5. Thus, in 145 hours at room temperature, 34% of 9,10-dichloroanthracene (III) was formed, with about 50% of the initial substance remaining unchanged; when the mixture was heated over a water bath for 3 hours, 9,10-dichloroanthracene was synthesized — 51.7% of the theoretical yield.



(III)

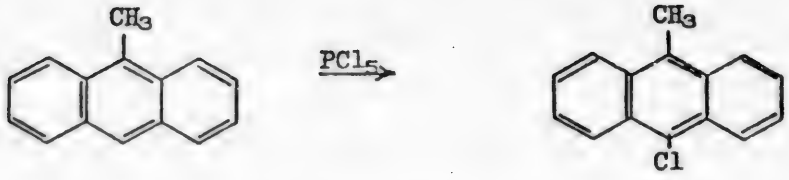
The reaction of 9-bromoanthracene with PCl_5 is even slower. At room temperature, with an excess of 0.2 equivalent of PCl_5, 17% of the theoretical yield of 9-chloro-10-bromoanthracene (IV) was synthesized in two days, with 70% of the initial substance being recovered unchanged.

Heating over a water bath for 3 hours yields 35% of chlorobromoanthracene, whereas 52% of 9-chloroanthracene is converted into 9,10-dichloroanthracene under these same conditions.



(IV)

The meso-homologs of anthracene — 9-methylanthracene — likewise reacts with PCl_5, and, like anthracene, this asymmetrical compound does not produce a phosphorus-organic compound, but rather a chloro derivative: 9-methyl-10-anthracene (V).

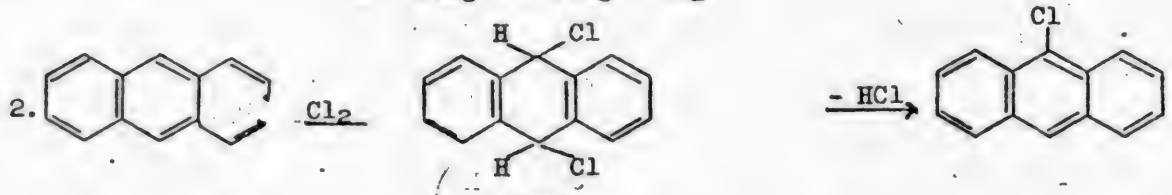


(V)

This last compound, not hitherto described, is prepared with a yield of 29% by allowing a mixture of hydrogen sulfide dissolved in benzene and PCl_5 to stand at room temperature for 24 hours.

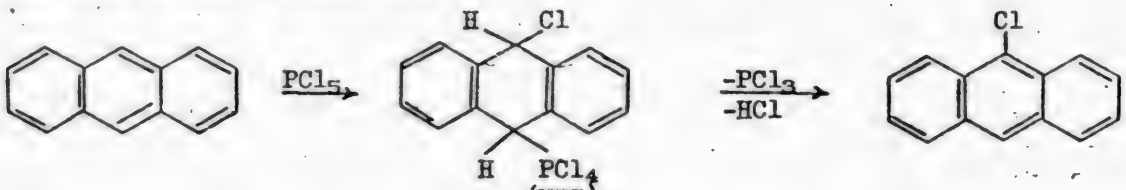
The mechanism of the reaction of anthracene and its derivatives with phosphorus pentachloride remains uncertain. It may be supposed that the reaction takes place via the preliminary dissociation of the PCl_5 into PCl_3 and chlorine, with the chlorine, like molecular chlorine, then being added to the molecule of the polycyclic compound, forming the dichloride (VI), which in turn, liberating hydrogen chloride, turns into the monochloro derivative.

1. $PCl_5 \rightarrow PCl_3 + Cl_2$



(VI)

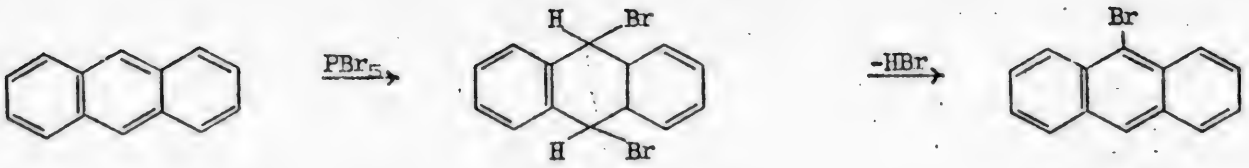
It is possible that only at high temperature (170-180°) is this sort of mechanism present in the formation of dichlorides from compounds that react with PCl_5, such as cinnamic acid and its derivatives [9], diphenylindene [10], and 1,2,-3,4--tetraphenylcyclopentodienone [2], i.e., when the phosphorus pentachloride undergoes considerable dissociation into chlorine and phosphorus trichloride [11]. When the reaction is effected at room temperature, with practically no dissociation of the phosphorus pentachloride, this mechanism is hardly likely. That is why we are inclined to support another possible reaction mechanism, in which a chlorine atom and PCl_4 are first attached to the molecule of anthracene or its derivative, after which the compound thus formed (VII) splits off PCl_3 and hydrogen chloride, turning into a chloro derivative.



(VII)

Exploration of the reaction of phosphorus pentabromide with anthracene and with some of the latter's derivatives has shown that here, as with phosphorus pentachloride, meso-halogen derivatives are produced.

When phosphorus pentabromide was added to a suspension of anthracene in benzene, the hydrocarbon was found to dissolve quickly, and within a few minutes a colorless, finely crystalline precipitate, 9,10-dibromo-9,10-dihydroanthracene (VIII) began to settle out. If the anthracene dibromide formed is not filtered out, it soon enters solution, being converted into 9-bromoanthracene (IX) by liberating hydrogen bromide. Compound (IX) can be recovered with a yield of 95.4%, based on the anthracene used.



(VIII) (IX)

When a slight excess of phosphorus pentabromide is used (0.2 equivalent), we get, in addition to the 9-bromoanthracene, 9,10-dibromoanthracene, which interferes with the purification of the monobromoderivative, though its own yield is only 74% under these conditions.

When isolated by itself, the anthracene dibromide (VIII) is unstable, evolving hydrogen bromide when left in an exsiccator. To convert all the dibromide in 9-bromoanthracene, there is no need to resort to Barnett's complicated method [12], which involves keeping a suspension of the dibromide in toluene, with a slight amount of phenol added, at room temperature for 4 days, after which it is heated to 50° and kept at that temperature for 2 hours, and then heated for half an hour over a water bath. According to our results, a 96% conversion of the dibromide into 9-bromoanthracene is readily achieved by heating it in benzene over a water bath until all the dibromide dissolves, which requires a few minutes when small quantities of the substance are used.

When phosphorus pentabromide is reacted with 9-bromoanthracene, 9,10-dibromoanthracene is formed. This reaction is slower than that with anthracene. Thus, during the course of an hour at room temperature, with 1.2 equivalents of phosphorus pentabromide employed, only 54% of the theoretical quantity of 9,10-dibromoanthracene is produced, 30% of the initial substance being recovered unchanged; after 24 hours under the same conditions, 84.6% of 9,10-dibromoanthracene can be recovered.

The reaction of 9-chloroanthracene and phosphorus pentabromide takes place at about the same rate as the latter's reaction with anthracene. When 1.2 equivalents of phosphorus pentabromide are reacted with a benzene solution of 9-chloroanthracene at room temperature, an 80% yield of 9-chloro-10-bromoanthracene is obtained within 20 minutes. This reaction is a simple preparative method for synthesizing 9-chloro-10-bromoanthracene. The latter compound was synthesized by Barnett and Cook [12] by reacting chlorine or sulfuryl chloride with 9-bromoanthracene. The authors do not indicate the yield, but it was obviously not high, since the crude reaction product required several crystallizations from various solvents for purification.

We also explored the reaction of 9-methylanthracene with phosphorus pentabromide, resulting in the formation of 9-methyl-10-bromoanthracene, with a yield that was 43% of the theoretical.

It should be pointed out that this compound, described by Barnett [13], is synthesized with an extremely poor yield by the direct action of bromine upon 9-methylanthracene.

The mechanism of the reaction of anthracene and its derivatives with phosphorus pentabromide doubtless boils down to a preliminary dissociation of the latter into bromine and phosphorus tribromide, with the ensuing addition of bromine to the aromatic compound and the further detachment of hydrogen bromide from the dibromide formed. This mechanism is supported by the ability of phosphorus pentabromide to undergo dissociation into bromine and phosphorus tribromide in organic solvents even at room temperature [14], as well as by our isolation of 9,10-dibromo-9,10-dihydroanthracene, the intermediate product of the addition of bromine to anthracene, by reacting phosphorus pentabromide with anthracene.

Evidently, the smoother formation of 9-methyl-10-bromoanthracene when phosphorus pentabromide acts upon 9-methylanthracene than when bromine reacts directly with 9-methylanthracene [13] is due to the fact that in the former case the bromine is present in such low concentrations in the reaction mass that the perbromination reactions of the initially formed 9-methyl-10-bromoanthracene (which take place when bromine is used directly) are negligible.

EXPERIMENTAL

Anthracene and Phosphorus Pentachloride; 9-Chloroanthracene

A mixture of 2 g of anthracene, 2.8 g of phosphorus pentachloride, and 25 ml of anhydrous benzene, placed in a small flask fitted with a reflux condenser and a calcium-chloride tube, was heated over a water bath for an hour. The substances dissolved after a few minutes heating, the solution turning an intense red. 0.6 g of crystals of 9-chloroanthracene: yellow needles with a m.p. of 104-106°, settled out of the solution upon cooling. The filtrate was washed with water, the solvent was driven off, and the residue was treated with boiling alcohol. The insoluble precipitate was filtered out and crystallized from benzene. This yielded 0.47 g of anthracene, with a m.p. of 215-217°. 1 g of 9-chloroanthracene, with a m.p. of 104-106°, crystallized out of the cooled alcoholic solution left after the anthracene had been separated out; another 0.05 g of the same substance, with a m.p. of 100-103° was recovered from the evaporated mother liquor. The yield of 9-chloroanthracene (1.65 g) constituted 69.3% of the theoretical.

The 9-chloroanthracene had a m.p. of 105-106° after recrystallization from alcohol. According to the literature 9-chloroanthracene melts at 106° [15].

In a test with 2 equivalents of phosphorus pentachloride (2 g of anthracene, 4.5 g of phosphorus pentachloride, and 50 ml of benzene), run at room temperature for 160 hours, we recovered 0.35 g of 9,10-dichloroanthracene (m.p. 208-210°) and 1.4 g of 9-chloroanthracene.

9-Chloroanthracene and Phosphorus Pentachloride; 9,10-Dichloroanthracene

A mixture of 1 g of 9-chloroanthracene, 1.9 g of phosphorus pentachloride, and 20 ml of benzene was heated for 3 hours over a water bath. The solution was then washed with water, and the solvent driven off. The residue was crystallized from acetone. This yielded 0.6 g (51.7%) of a substance, consisting of yellow needles with a m.p. of 207-209°. After recrystallization the substance had a m.p. of 210-211° and exhibited no depression when mixed with a sample of 9,10-dichloroanthracene. 0.2 g of the initial chloroanthracene was recovered from the mother liquor.

In a second experiment, run with the same quantities of the initial substances, the reaction mixture was set aside to stand for 6 days at room temperature. This yielded 0.4 g of 9,10-dichloroanthracene (34.4%) and 0.5 g of the initial monochloro derivative.

9-Bromoanthracene and Phosphorus Pentachloride; 9-Chloro-10-Bromoanthracene

A mixture of 4 g of 9-bromoanthracene, 5.8 g of phosphorus pentachloride, and 60 ml of benzene was heated for 3 hours over a water bath. The solution was washed with water, the solvent was driven off, and the residue treated with hot alcohol. 2.55 g of the initial 9-bromoanthracene was recovered from the alcoholic solution, separated from the insoluble constituents. The residue insoluble in alcohol was crystallized from benzene. This yielded 1.6 g (35.5%) of 9-chloro-10-bromoanthracene as yellow crystals with a m.p. of 208-210°. After recrystallization from benzene the substance had a m.p. of 210.5-211°. Barnett and Cook [12] synthesized this substance in a less pure state (m.p. 207°) by reacting chlorine and 9-bromoanthracene.

9-Methylanthracene and Phosphorus Pentachloride; 9-Methyl-10-chloroanthracene

1.3 g of phosphorus pentachloride was added to a solution of 1 g of 9-methylanthracene in 25 ml of benzene, and the reaction mixture was set aside to stand at room temperature for 19 hours. During this time all the phosphorus pentachloride dissolved. The solution was washed, the solvent driven off, and the residue treated with hot acetone. The insoluble precipitate was filtered out, and the mother liquor was cooled. This yielded 0.25 g of a substance with a m.p. of 173-176°.

Another 0.12 g of the substance, with a m.p. of 172-176°, was isolated from the partially evaporated mother liquor. Crystallization of both fractions from alcohol yielded 0.35 g of 9-methyl-10-chloroanthracene as light yellow small needles; m.p. 179-180°. The yield was 29.6% of the theoretical.

2.985 mg substance: 8.703 mg CO_2; 1.396 mg H_2O.
Found %: C 79.56; H 5.23.
$C_{15}H_{11}Cl$. Calculated %: C 79.47; H 4.89.

Anthracene and Phosphorus Pentabromide; 9-Bromoanthracene

a) Phosphorus pentabromide (5.07 g) was added to a suspension of anthracene (2 g) in 50 ml of benzene. The hydrocarbon dissolved quickly, and soon a finely crystalline powder of anthracene dibromide began to separate out, but it subsequently disappeared gradually. The reaction was complete twenty minutes after the start of the experiment. The solution was washed with water, the benzene driven off, the residue dissolved in alcohol with heating, and the solution filtered to remove the small quantity of insoluble impurities. 2.4 g of 9-bromoanthracene, m.p. 100-101°, crystallized out of the cooled solution; another 0.35 g of bromoanthracene with a somewhat poorer m.p. (97-100°) was recovered from the partially evaporated mother liquor. The yield was 95.4% of the theoretical.

b) The same quantities of the substances were taken as in the foregoing experiment. Ten minutes after the start of the experiment the finely crystalline powder that settled was filtered out, washed with benzene and ether, and desiccated in vacuum. M.p. 94-97°. It exhibited no depression of the melting point when mixed with a sample of 9,10-dibromo-9,10-dihydroanthracene, prepared by reacting bromine with anthracene dissolved in hydrogen sulfide.

When heated for a short time in benzene, 96.2% of the synthesized substance is converted into 9-bromoanthracene.

9-Chloroanthracene and Phosphorus Pentabromide; 9-Chloro-10-bromoanthracene

Phosphorus pentabromide (2.4 g) was added to a solution of 9-chloroanthracene (1 g) in benzene (20 ml) and the reaction mixture was set aside to stand at room temperature for 20 minutes, with periodic shaking. The crystals that separated out were filtered out and recrystallized from alcohol. This yielded 0.6 g of a substance with a m.p. of 210.5-211°. The initial benzene solution was washed with water, the solvent was driven off, and the residue was recrystallized from alcohol. Another 0.5 g of 9-chloro-10-bromoanthracene with a m.p. of 210.5-211°. The yield of the substance totaled 80.2% of the theoretical.

9-Bromoanthracene and Phosphorus Pentabromide; 9,10-Dibromoanthracene

2 g of phosphorus pentabromide was added to a solution of 1 g of 9-bromoanthracene in 15 ml of benzene, and the reaction mixture was set aside to stand for 24 days at room temperature. The 9,10-dibromoanthracene recovered (0.9 g, m.p. 220-221°) was filtered out, and the filtrate was washed with water and concentrated down to small volume. Another 0.2 g of the substance, with a m.p. of 218-220°, was recovered. The yield totaled 84.6%.

9-Methylanthracene and Phosphorus Pentabromide; 9-Methyl-10-bromoanthracene

2.7 g of phosphorus pentabromide was added to a solution of 1 g of 9-methylanthracene in 20 ml of benzene. After 10 minutes of stirring all the phosphorus pentabromide entered into solution. The reaction mixture was washed with water, the solvent was driven off, and the residue was treated with hot alcohol until the crystalline mass dissolved.

0.6 g of 9-methyl-10-bromoanthracene, with a m.p. of 170-173°, representing 42.5% of the theoretical quantity, was recovered from the alcoholic solution combined with the undissolved oil.

Barnett [13] gives 173° as the m.p. of 9-methyl-10-bromoanthracene.

SUMMARY

1. Anthracene, 9-methylanthracene, and the 9-halogen substitution derivatives of anthracene react with phosphorus pentachloride in benzene to form the corresponding mesochloro derivatives.

2. The reaction of anthracene with phosphorus pentabromide in benzene yields 9,10-dibromo-9,10-dihydroanthracene, which is then converted into 9-bromoanthracene by splitting off hydrogen bromide.

Under the action of phosphorus pentabromide, 9-methylanthracene and 9-halogen substitution derivatives of anthracene yield the corresponding mesobromo derivatives.

3. The reaction of anthracene and its derivatives with phosphorus pentabromide boils down to the preliminary dissociation of the latter into bromine and phosphorus tribromide, followed by the addition of bromine to the aromatic compound and the ensuing splitting off of hydrogen bromide from the resulting dibromide.

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Received July 11, 1948.

RESEARCHES ON HYDROXYFUCHSONE DYES

XI [1] THE OXIDATIVE-ALKALINE DECOMPOSITION OF HYDROXY-FUCHSONE DYES OF THE BENZAURIN GROUP

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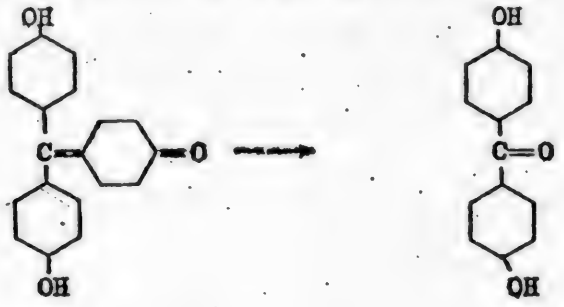
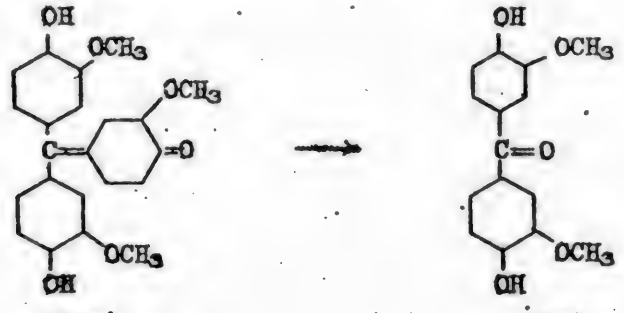
It was long ago noticed that aurin (I) decomposes when heated with water in sealed tubes [2] or when air or oxygen is passed through an alkaline solution of the dye [3]. In both cases 4,4'-dihydroxybenzophenone (II) is formed; in addition, hydrolysis gives rise to phenol, and alkaline aeration gives rise to quinone, which breaks down under the experimental conditions



(I) (II)

I.Y.Postovsky and A.M.Eidlin [4] have established that aurin is most most easily cleaved by passing air or oxygen through an alkaline solution of the dye heated to 100°, and that under these conditions the methoxy derivatives of aurin are also cleaved, though much more slowly; by this method 3,3'-dimethoxy-4,4'-dihydroxybenzophenone (IV), hitherto unknown, was synthesized from rubrocol (III).



(III) (IV)

According to Postovsky and Eidlin, in this oxidative cleavage of hydroxyfuchsone dyes, the first compound to be formed is a not very stable product (which has not been isolated) of the addition of oxygen at the double bond that connects the

central triphenylmethane carbon to the quinoid ring. This intermediate product of the peroxide type then breaks down further into the respective substitution products of benzophenone and quinone as follows:

But in neutral organic solvents, when the hydroxyfuchsone dyes possess an oxyquinone structure, no noticeable oxidative cleavage takes place; this was noticed by Postovsky and Kidiin and has been confirmed by our observations. Oxidative cleavage takes place rapidly in alkaline solutions, which contain, not an oxyquinone form of the dye, but a much more deeply colored and, to a certain degree, unsaturated mesomeric anion.

The mechanism of and the optimum conditions for such decomposition of hydroxyfuchsone dyes are worthy of study. (It is quite probable, as Postovsky supposes, that when rubrocal is employed in chemotherapy, it is not the dye itself that displays activity, but its cleavage products formed within the organism.) It was of interest in this connection to determine whether the course of this process is related to the concentration of alkali in the solution; this problem was not considered by Postovsky and Kidiin.

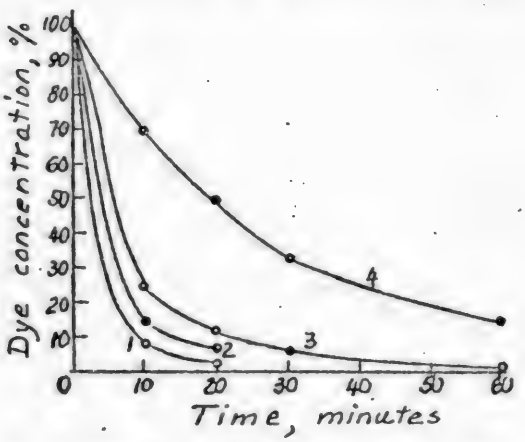


Fig. 1. Cleavage of aurin in alkaline solutions.

1-NaOH 5%; 2-NaOH 1%; 3-NaOH 0.1%; 4-Na_2CO_3 1%.

To solve this problem it was necessary to find a method for quantitatively determining hydroxyfuchsone dyes as their oxidative decomposition proceeded in alkaline solutions of various concentrations. After a number of attempts, we settled upon the following method: we passed oxygen from a tank through dilute alkaline solutions of the dye heated over a boiling water bath; at fixed intervals of time we took exact samples of the solution and acidulated them with 10% hydrochloric acid, used in considerable excess, after which the color intensity of the stable colored dye cation that was formed was compared colorimetrically with a standard. In control experiments we convinced ourselves that with the diluted dyes employed, the presence of substances formed as a result of the decomposition of the dyes had absolutely no effect upon the precision of measurement.

The results obtained are cited in the experimental section and are shown graphically in the curves of Figs. 1 and 2.

Figure 1 contains the curves showing the rate of alkaline aeration of aurin at various alkali concentrations and in a 1% soda solution. As these curves indicate, increasing the concentration of alkali results in an increase in the rate of oxidative cleavage of aurin. This is even clearer from an examination of the curves in Fig. 2, showing the course of this process for rubrocal, which is cleaved more slowly than aurin, other conditions being the same.

We resolved to supplement these experiments by a study of the oxidative-

alkaline decomposition of benzaurin dyes, we employed the same method of determining the reaction velocity as that described above for aurin and rubrocol. Our experiments indicated that in a soda solution and in dilute alkaline solutions, benzaurin and 3,3'-dimethoxybenzaurin [5] undergo oxidative cleavage much more quickly than do aurin and trimethoxyaurin. This may be seen by comparing the curves of Figs. 3 and 4. These figures make it clear that the presence of the methoxyl groups retards cleavage both in the aurin and the benzaurin dye groups.

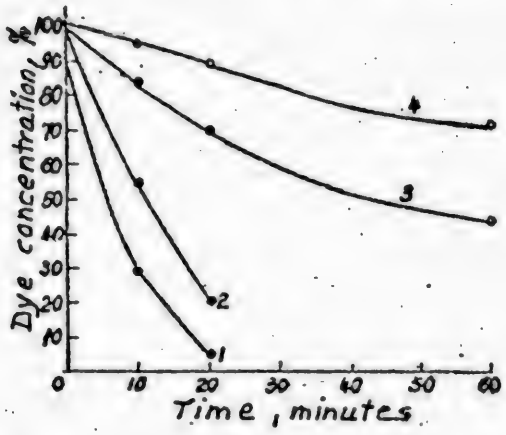


Fig. 2. Cleavage of trimethoxyaurin in alkaline solutions.

1-NaOH 5%; 2-NaOH 1%; 3-NaOH 0.1%; 4-Na_2CO_3 1%.

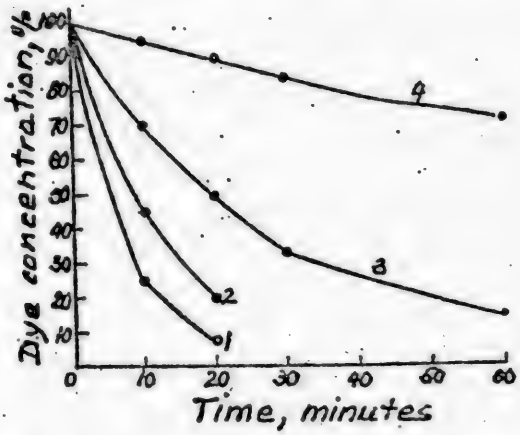


Fig. 3. Cleavage of hydroxyfuchsone dyes in 1% NA_2CO_3.

1-Benzaurin; 2-dimethoxybenzaurin; 3-aurin; 4-trimethoxyaurin.

But when the alkali concentration was increased, we found that the rate of oxidative cleavage dropped in the benzaurin group of dyes, as contrasted with the above-described experiments with aurin dyes. In a 1% solution of sodium hydroxide this process is slower than in a 0.1% solution; the oxidative cleavage of benzaurin and its dimethoxy derivative is practically nonexistent in a 5% solution of sodium hydroxide. But deeper analysis made it possible to explain the reason for this difference in the effect of alkali concentration upon the rate of oxidative cleavage of hydroxyfuchsone dyes of the aurin and benzaurin groups.

In one of our preceding reports [6], we pointed out that dyes of the benzaurin group are converted into the salt of a colorless carbinol derivative at much lower alkali concentrations than dyes of the aurin group. In 5% solutions of sodium hydroxide, benzaurin and its derivatives are wholly converted into salts of carbinol derivatives, the latter containing no quinoid groups and thus being stable against oxidative

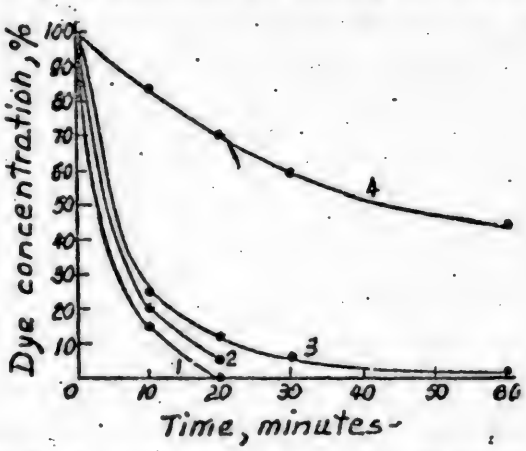


Fig. 4. Cleavage of hydroxyfuchsone dyes in 0.1% NaOH.

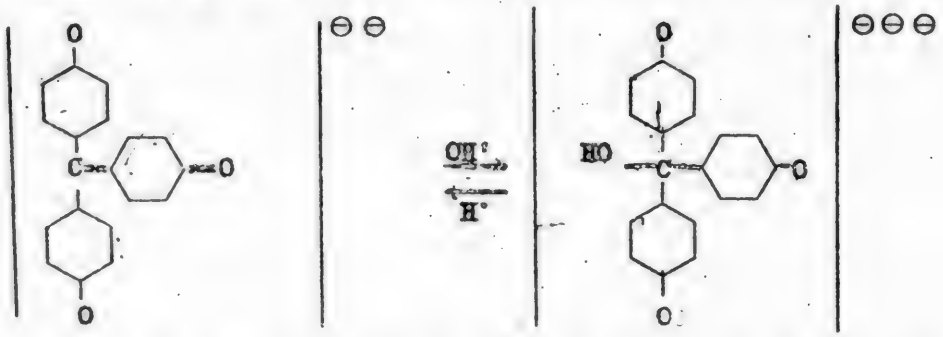
1-Benzaurin; 2-dimethoxybenzaurin; 3-aurin; 4-trimethoxyaurin.

cleavage. Only the colored mesomeric and, to a certain degree, unsaturated anions of dyes, which are formed in the benzaurin group only in soda solutions or in dilute alkali solutions, undergo this kind of cleavage.

Thus, there are two rival processes in the oxidative-alkaline cleavage of hydroxyfuchsone dyes. One of them involves the actual cleavage of a colored mesomeric dye anion that is unstable in the presence of the oxidant; the other results in the conversion of this colored anion into a colorless anion of a carbinol derivative, which resists oxidative cleavage. Increasing the alkali concentration speeds up the first process while at the same time it facilitates the conversion of the dye into a carbinol derivative, which resists oxidative cleavage. [illegible] at the same time. [illegible]. In the aurin series, higher concentrations of alkali are required to form carbinol derivatives; this takes place in the benzaurin series at lower alkali concentrations, and as a result we get the impression that increasing the alkali concentration retards the process of dye cleavage and practically stops it in strong alkalies.

We detected this effect of an alkali only thanks to the experimental method we employed. Had we judged the course of the reaction solely by the decolorizing of an alkaline solution or by the quantity of oxygen absorbed [4], we would have obtained the wrong impression; by acidulating alkaline solution with strong hydrochloric acids, when an as yet uncleaved anion of the dye and the synthesized carbinol derivative are converted into a colored cation, we are able to make a quantitative determination of the degree of actual oxidative-alkaline cleavage of the dye.

We take this opportunity to correct an error in one of our cited reports [6]. In our study of the conversion of hydroxyfuchsone dyes in the alkaline zone we used more highly concentrated solutions of the dyes and came to the conclusion that the formation of carbinol derivatives is an irreversible process. Repeating this research with dilute dye solutions, we found that this process is reversible and that in alkaline solutions an equilibrium is reached between the colored mesomeric anion of the dye and the anion of the colorless carbinol derivative, in accordance with the following diagram (for aurin):



This equilibrium is shifted toward the carbinol derivative as the alkali concentration is increased. The state of equilibrium also depends upon the temperature factor; raising the temperature converts the anion of the carbinol derivative into the colored anion of the dye. This may be proved by means of the following simple and very striking experiments, which may be easily employed for lecture demonstrations. Aurin may be used for this purpose, though 5,5'-dimethoxybenzaurin is even better. 1 ml of a 0.1% solution of aurin is placed in 20 ml of a 10% solution of sodium hydroxide. When the mixture is chilled to 0°, the solution is almost completely decolorized; at 25° the solution turns pink; and when heated to 100°, the solution becomes an intense red. When the solution is again chilled to 0°, it is again decolorized, and this change in color may be repeated ad lib. But alkaline

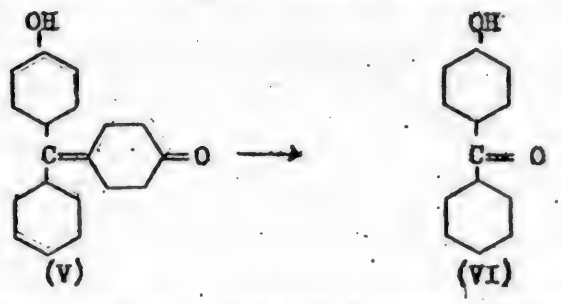
aeration quickly takes place in the heated colored solution, especially at low dye concentrations, as a result of which the dye is gradually cleaved.

These reversible transformations of the colored anion of the dye into the carbinol derivative are even more striking in the case of 3,3'-dimethoxybenzaurin. Nor need the alkali be as strong in this case. It is most convenient to add 1 ml of 0.1% solution of the dye to 20 ml of 0.5% sodium hydroxide. When cooled to 0°, the solution is decolorized quickly and completely; at 25° it turns sky-blue; and at 100° an intense blue. It is again decolorized by chilling it to 0°. But, in this case the oxidative cleavage of the dye also takes place even more rapidly than before, when heated solutions are allowed to stand.

Owing to this effect of the temperature factor on benzaurin and 3,3'-dimethoxybenzaurin, their dilute solutions in 1% caustic soda are completely colorless when chilled though air or oxygen are passed through them, but when heated to 100°, with the equilibrium thus shifted toward the colored dye anion, they undergo oxidative cleavage fairly rapidly, though somewhat more slowly than in 0.1% alkali. In 5% alkali, solutions of dyes of the benzaurin group remain colorless even when heated, which is why oxidative cleavage is hardly noticeable.

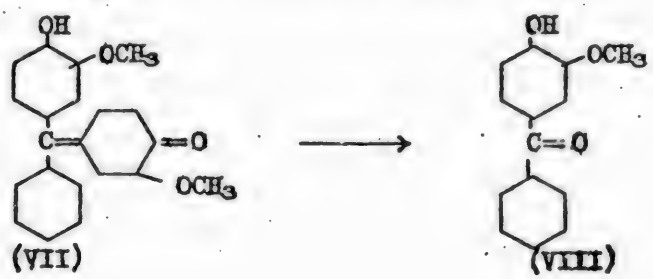
For final corroboration of the foregoing comparisons of the oxidative-alkaline cleavage of dyes of the aurin and benzaurin groups, it should be proved that in both of these groups cleavage takes place in the same direction, forming correspondingly arranged derivatives of benzophenone. We therefore effected the alkaline aeration of benzaurin and 3,3'-dimethoxybenzaurin – with a view of preparative procedures – in more highly concentrated solutions; in the light of the experiments described above, we departed from the cleavage of aurin and carried out the process in a weaker solution, 1% of sodium hydroxide.

From the unsubstituted benzaurin (V) we thus synthesized 4-hydroxybenzophenone (VI), which was identified with the substance synthesized (by Doebner's method [7]) by reacting benzoyl chloride with phenyl benzoate and then saponifying the resulting ester.



(V) (VI)

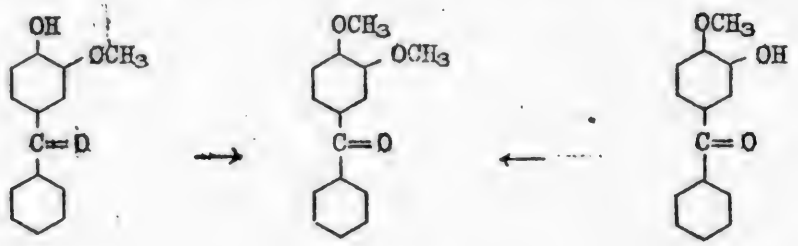
3,3'-dimethoxybenzaurin (VII) yielded a cleavage product that crystallized as colorless lamellae, with a m.p. of 97-98°, from aqueous alcohol. The structure of 3-methoxy-4-hydroxybenzophenone (VIII) should be ascribed to this substance by analogy with the cleavage product of benzaurin described above and as the result of analytical determinations.



(VII) (VIII)

The synthesis of this derivative of benzophenone enables us to solve the problem of the structure of the substance first synthesized by Bartolotti [8] when he condensed benzoyl chloride with guaiacol in the presence of zinc chloride. A benzoate is formed, which upon saponification yielded hydroxymethoxybenzophenone, which crystallizes as needles with a m.p. of 131-132° from aqueous alcohol. When he methylated this substance with methyl iodide, Bartolotti synthesized 3,4-dimethoxybenzophenone (IX), which was found to be identical with the products of the oxidation of

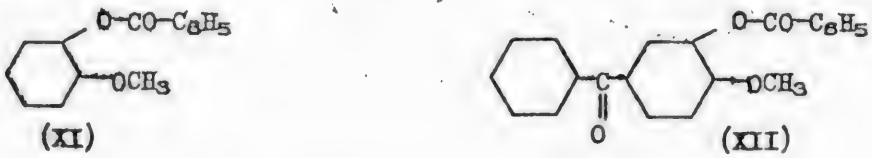
3,4-dimethoxydiphenylmethane, described by Koenig and Kostanecki [8]. In view of this Bartolotti assumed that the benzophenone derivative he had synthesized by benzoylating guaiacol had to have either structure (VIII) or (X).



(VIII) (IX) (X)

Repeating Bartolotti's research, we obtained the substance he had described: crystalline needles with a m.p. of 131-132°. The cleavage product of 3,3'-dimethoxybenzaurin (VII), which has the undisputed structure (VIII), crystallizes as lamellae with a m.p. of 97-98°. A mixture of these two substances begins to fuse at 75-78°. When both substances were treated with dimethyl sulfate, we got the same dimethoxy derivative (IX), which crystallized as tiny needles with a m.p. of 99-100° from aqueous alcohol. This was further proof of structure (VIII) for the cleavage product of 3,3'-dimethoxybenzaurin and, moreover, we have established beyond doubt that the product of the benzoylation of guaiacol with a m.p. of 131-132°, described by Bartolotti, has the structure of 3-hydroxy-4-methoxybenzophenone (X).

It may be found rather strange that in the benzoylation of guaiacol the benzoyl radical chiefly takes a para position to the hydroxyl group rather than to the methoxyl group. It should be borne in mind, however, that in the first stage of this reaction guaiacyl benzoate (XI) is formed, in which the methoxyl group is a more active Class I substituent than the ester group. That is precisely why the major product of the benzoylation of guaiacol is the benzoate of 3-hydroxy-4-methoxybenzophenone (XII), from which 3-hydroxy-4-methoxybenzophenone (X) is obtained by saponification.



(XI) (XII)

EXPERIMENTAL

A. Comparison of the Rates of Oxidative Cleavage of Hydroxyfuchsone Dyes of the Aurin and Benzaurin Groups

10 ml of a 0.1% solution of the dye in a 1% solution of soda was added to 100 ml of alkaline solution of given concentration, placed in a tall beaker fitted with

a bubbler and heated over a boiling water bath. 5 ml of the resulting colored solution was taken, and 20 ml of 15% hydrochloric acid was added to this sample. The resulting stable colored solution of the onium salt of the dye served as a standard for subsequent colorimetric comparisons.

Then a current of oxygen from a tank was passed via the bubbler (in excess, at the rate of 2 liters in 10 minutes) through an alkaline solution of the dye, heated over a water bath; every 10 minutes a 5-ml sample was taken and immediately added to 20 ml of 15% hydrochloric acid. The concentration of dye in the resulting solution is determined by the intensity of the color as compared in the colorimeter with that of the standard solution described above (when the dye is completely cleaved, we get a wholly colorless solution; this indicates that at this dye concentration the dye cleavage products produce no distortion of the colorimetric measurements).

The results obtained are listed in the following table.

Rate of Oxidative-Alkaline Cleavage of Hydroxyfuchsone Dyes as a Function of the Alkali Concentration

Tested Dye	Color intensity	Na_2CO_3 1%	NaOH 0.1%	NaOH 1%	NaOH 5 %
Aurin.....	Initial concentration	100	100	100	100
	After 10 minutes	70	25	14	8
	After 20 minutes	50	12	6	3
	After 30 minutes	33	6	–	–
	After 60 minutes	15	3	–	–
Trimethoxyaurin...	Initial concentration	100	100	100	100
	After 10 minutes	95	84	55	29
	After 20 minutes	90	70	20	5
	After 30 minutes	84	60	–	–
	After 60 minutes	72	45	–	–
Benzaurin.....	Initial concentration	100	100	100	100
	After 10 minutes	28	15	20	100
	After 20 minutes	8	0	4	100
Dimethoxybenzaurin	Initial concentration	100	100	100	100
	After 10 minutes	45	20	32	100
	After 20 minutes	20	6	10	100

B. Preparative Cleavage of Benzaurin and 3,3'-Dimethoxybenzaurin

I. Alkaline Aeration of Benzaurin; Synthesis of 4-Hydroxybenzophenone

5 g of benzaurin are dissolved in 250 ml of a 1% solution of sodium hydroxide, and air that has been first passed through a tube filled with soda lime is drawn through the solution while the latter is heated over a water bath. The purple color of the solution gradually turns brownish-red, after which the reaction is broken off. 10 ml of acetic acid and 2 ml of sodium bisulfite are added to the hot solution, which is then chilled. The gray precipitate that settles out is crystallized from dilute alcohol in the presence of a small quantity of the bisulfite. This yields 1.5 g of 4-hydroxybenzophenone as crystalline colorless platelets with a m.p. of 134-135°. After crystallization from alcohol the benzoate of the substance had a m.p. of 112.5°.

II. Alkaline Aeration of 3,3'-Dimethoxybenzaurin

Synthesis of 3-methoxy-4-hydroxybenzophenone. 5 g of the dye is dissolved

in 300 ml of a 1% solution of sodium hydroxide and a current of air that has first passed through a tube filled with soda lime is drawn through the solution while the latter is heated over a water bath. In this case the process takes more time than in the reaction of benzaurin. The bluish-purple solution finally turns brownish-red, and the reaction is brought to a stop. 20 ml of acetic acid and 2 ml of bisulfite are added to the solution. The precipitate that settles out is crystallized from aqueous alcohol to which a small amount of bisulfite has been added; the reaction product separates out as colorless crystalline platelets with a m.p. of 97-98°.

Properties of 3-Methoxy-4-hydroxybenzophenone. Colorless platelets with a m.p. of 97-98°; soluble in hot water, and in alcohol, ether, and acetic acid; soluble in alkalies, forming yellow solutions.

0.1256 g substance: 0.3396 g CO_2; 0.0580 g H_2O.
Found %: C 73.77; H 5.13.
$C_{14}H_{12}O_3$. Calculated %: C 73.68; H 5.26.

Comparison with 3-Hydroxy-4-methoxybenzophenone. A mixture of 10 g of guaiacol, 15 g of benzoyl chloride, and 8 g of zinc chloride is heated for 2 hours over a water bath, after which 100 ml of water is added to the reaction mass. The resulting oil solidifies when chilled; it is separated from the solution and crystallized from aqueous alcohol. This yields 3-hydroxy-4-methoxybenzophenone benzoate, as crystalline lamellae with a m.p. of 96°. This benzoate is saponified by boiling it with an aqueous alkali, the hydroxymethoxybenzophenone being precipitated from the resulting solution by adding acetic acid. The precipitate is crystallized from aqueous alcohol; this yields colorless crystalline needles of 3-hydroxy-4-methoxybenzophenone, with a m.p. of 131-132°.

0.5 g of each of the hydroxymethoxybenzophenones, with m.p. of 97-98° and 131-132°, is dissolved in 10 ml of 10% sodium hydroxide solution, and 1 ml of dimethyl sulfate is slowly added to each of the heated solutions; toward the end of the reaction, the solutions should be alkaline, as indicated by their yellow color. At the end of the reaction oily drops, which harden upon congealing, collect at the bottom of both vessels. Without separating them, each solution is shaken up three times with 10 ml of ether, the ether being blown off the combined ether layers after filtration through a dry filter. This results in the precipitation of a white deposit, which fuses at 96-98° and is recovered as the acicular crystals of 3,4-dimethoxybenzophenone, with a m.p. of 99-100° after crystallization from aqueous alcohol. A mixture of the crystals separately obtained from each of the hydroxymethoxybenzophenones described above likewise fuses at 99-100°.

SUMMARY

1. The alkaline aeration of the hydroxyfuchsone dyes of the benzaurin and aurin groups yields the corresponding substitution derivatives of benzophenone: 4-hydroxybenzophenone from benzaurin, and the hitherto undescribed 3-methoxy-4-hydroxybenzophenone, which crystallizes as colorless lamellae with a m.p. of 97-98°, from 3,3'-dimethoxybenzaurin.

2. Isolation of this derivative of benzophenone made it possible to establish the structure of the substance first synthesized by Bartolotti when he reacted benzoyl chloride with guaiacol, which crystallizes as colorless needles with a m.p. of 131-132°. This benzoyl guaiacol must have the structure of 4-methoxy-3-hydroxybenzophenone; it follows that when guaiacol is benzoylated, the intermediate product being guaicyl benzoate, the benzoyl radical is chiefly in a para position to the methoxyl group rather than to the ester group.

3. The colored mesomeric anions of dyes undergo oxidative-alkaline decom-

position; solutions of dyes in the undissociated oxyquinone form, as well as solutions of salts of their colorless carbinol derivatives, resist oxidative-alkaline decomposition.

4. When the alkali concentration is raised, the rate of oxidative decomposition rises; but when the concentration of alkali in the solution rises, the quantity of carbinol derivative stable against cleavage also increases, causing the impression that the cleavage process itself is slowed down. This is especially noticeable in the benzaurin series, in which carbinol derivatives are formed in weaker alkaline solutions.

5. By way of supplementing a previous report [6], it is noted that the colored mesomeric anion of the dye and the colorless anion of the carbinol derivative are in equilibrium in alkaline solutions of hydroxyfuchsone dyes; this state of equilibrium depends on the alkali concentration and the temperature: an increase in alkali strength or a reduction in temperature shifts the equilibrium toward the carbinol derivative; At lower alkali concentrations or at higher temperatures the equilibrium is shifted toward the colored dye anion.

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June 12, 1948

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A NEW METHOD OF SYNTHESIZING POLYPEPTIDES BY CONDENSING THE AMIDES OF HYDROXY ACIDS

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The synthesis of polyamide resins has undergone considerable evolution since the time of Carothers' first researches [1], and today it has become a fully-developed branch of chemistry. But the most interesting of the polyamides – the polypeptides, in which the peptide bonds alternate along the chain in the alpha position to the carbon atoms, have attracted undeservedly little attention. They are important because they are synthetic analogs and models of the proteins and may be of considerable aid in clearing up the structure of these most complicated substances in nature.

Ever since the time of Emil Fischer, very little success has been achieved in the synthesis of polymer peptides. We know that Fischer [2] succeeded, by means of a step-by-step synthesis, in producing a chain consisting of 7 amino acid groups. He was first to discover that esters of the tripeptides can be condensed when heated to high temperature. Fischer's esters of the amino acids and the lower peptides were later employed by Katchalski [3] and Pacsu and associates [4,5]; the latter succeeded in synthesizing polyglycines with a polymerization number as high as 90 from the esters of the tripeptides; these polyglycines were horny resins insoluble in water, with the intensive hydrogen bonds between the chains producing something like the structure of a three-dimensional polymer.

Polymers of the more complicated amino acids may well be of much greater interest. The presence of side chains interferes with the formation of hydrogen bonds between the chains. This circumstance ought to increase the solubility of polymers and facilitate the spherical structure of the macromolecules that is typical of proteins, as has been set forth in detail in the paper by Bresler and Talmud [6].

In 1947 Woodward and Schramm [7] were the first to synthesize polypeptides of high molecular weight by polymerizing and copolymerizing Leuchs anhydrides, leucine, and phenylalanine.

In synthesizing polypeptides, we made use of the condensation of the amide and alcohol groups, which occurs at relatively mild temperatures under the action of metallic sodium.

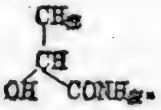
$$R_1CONH_2 + R_2OH \longrightarrow R_1CONHR_2 + H_2O. \qquad (1)$$

This reaction has apparently not been the subject of investigation up to the present, notwithstanding its simplicity. At any rate, there is no mention of it, even in the most comprehensive monographs on the chemistry of the amides (e.g., Sidgwick's Organic Chemistry of Nitrogen, 1945).

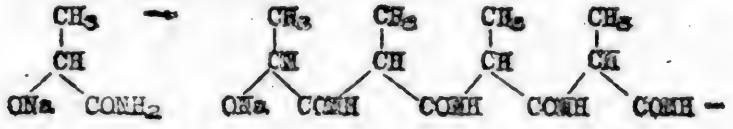
We began by carrying out this reaction with the simplest compounds: acetamide and ethyl alcohol:

$$CH_3CONH_2 + C_2H_5OH \longrightarrow CH_3CONHC_2H_5 + H_2O \qquad (2)$$

The synthesis process was as follows: 40 g of acetamide was added to 100 ml of absolute alcohol, dissolving completely. Then 11.5 g of sodium alcoholate was added, and the reaction mixture was heated to the boiling point of alcohol over a water bath, with a reflux condenser. A crystalline substance settled out as a precipitate very quickly (20-30 minutes). To purify the product and free it of any sodium alcoholate, the whole reaction mixture was dissolved in an excess of absolute alcohol, after which the solution was saturated with anhydrous HCl. This caused all the sodium to precipitate as NaCl, which is insoluble in absolute alcohol. Evaporation of the alcohol yielded the pure crystalline product of the synthesis, which proved to be ethylacetamide hydrochloride, $CH_3CONHC_2H_5 \cdot HCl$, (m.p. 59°). The yield was close to the theoretical. The usual method of synthesis of this compound described in the literature [8] involves many stages via halogen derivatives and requires incomparably more labor and time. But, most important of all, we discovered that reaction (1) is completed smoothly and, apparently, without the formation of any by-products. We then turned to our fundamental task – the synthesis of the polypeptides. We undertook as our first example the synthesis of polyalanine, starting with the amide of lactic acid,



We prepared lactamide from commercial lactic acid in two stages by the method described in the literature [9]. First we prepared ethyl lactate by esterifying the acid in the presence of anhydrous $CuSO_4$ as the dehydrating agent. After the ester had been purified by distillation, it was converted into the amide by reacting it with liquid ammonia. The amide is a hygroscopic crystalline substance that is readily soluble in water and alcohol, and – as we discovered, in dioxane. We used a solution of lactamide in dioxane to prepare the alcoholate. The dioxane solution of the amide was boiled with a reflux condenser in the presence of metallic sodium, which converted it into the alcoholate; the latter immediately settled out of the solution as a compact crystalline mass (m.p. 26°). This compound served us as the initial monomer for the polycondensation reaction. In the light of our research on the reaction of acetamide with alcohol, we might expect the polycondensation reaction to proceed as follows:



$$+ nNaOH. \qquad (3)$$

The experimental conditions were: 8 g of the Na-substituted amide were sealed into an ampoule from which the air had been exhausted by a vacuum pump. The ampoule was heated to 80° for 3-4 weeks in a thermostat; its contents turned into a solid, transparent, slightly yellowish resin.

The ampoule was opened, and its contents dissolved in absolute alcohol (100 ml), anhydrous HCl being passed through the solution to eliminate the sodium. All the latter settled out as NaCl, which was proved by testing the solution for ash content. The sodium chloride was filtered out of the solution (ca. 100 ml), which was then decolorized with a small amount (3 g) of activated charcoal (Norite), and the alcohol was driven off in vacuum. This yielded a hard, amorphous, transparent resin, which decomposed without fusion at ~ 105° after being washed with ether and subjected to Carothers' purification in high vacuum.

Our polymer was insoluble in ether, dioxane, or acetone, but it dissolved readily in water and less so in ethyl alcohol.

When polymerization was effected in a shorter interval (5-7 days), the resulting resin was not as hard, which indicated a lower degree of polymerization.

We also tried to carry out the reaction heterogeneously: we sealed the unsubstituted lactamide in the ampoule with metallic sodium and heated it to 110° – above the melting point of sodium. Polycondensation took place under these conditions, but the product turned quite dark and partially decomposed, as was indicated by the strong odor of ammonia noticed when the ampoule was opened. Sometimes the ampoules burst open, evidently because of the generation of gaseous hydrogen.

To determine the structure of our polymer, we proceeded exactly as is done with proteins: we subjected our product to cleavage by acid and an alimentary ferment, and then analyzed the hydrolysis products. We were able to demonstrate, by two independent methods, that the products of the polymer's hydrolysis consist principally of alanine. This proved that our polymer is a polyalanine, in accordance with our Equation (3). The circumstance that our polymer is easily attacked by an alimentary ferment (a commercial preparation of pancreatine) leaves no doubt concerning the fact that the alanine groups in the chain are linked together by peptide bonds. Hence, this doubtless is a polymer polypeptide, with only the ends of the macromolecule chain containing the $CONH_2$ and OH groups instead of the amine and carboxyl groups.

Let us dwell on some details of the experiments. The acid hydrolysis of the polymer was effected as follows: 0.0985 g of the polymer was dissolved in 1 g of concentrated HCl. The solution was transferred to an ampoule and washed with 1 ml of absolute alcohol. The ampoule was kept at a temperature of 36° for 22 hours in a thermostat. We then determined the amino nitrogen (by the van Sluijk method) and the total nitrogen (by the Kjeldahl method); this was also done before hydrolysis started. The results are listed below.

	Theoretical value, based on infinite polymerization	Polymer before hydrolysis	Polymer after hydrolysis
		Experimental, per cent	
Amino nitrogen	0	0	6.1
Total nitrogen	18.3	14.30	14.3

Thus, the initial polymer contains no amino nitrogen, as we had supposed; as for the total nitrogen, it is somewhat below the figure that should be found for infinitely deep polymerization. The amino nitrogen measured after hydrolysis corresponds to the decomposition of 40% of the polymer's peptide bonds.

The experiment on the fermentative hydrolysis of the polymer was made as follows: 0.05 g of the polymer was dissolved in 50 ml of a borate buffer with a pH of 7.8 and placed in a thermostat at 36°. One hour later 0.005 g of the ferment was added (the commercial Merck preparation of pancreatine). Periodic samples were then taken and analyzed (van Sluijk method) for amine nitrogen. The curve of the cleavage kinetics of our polypeptide is shown in Fig. 1 (the ordinates are the quantity of amino nitrogen generated per ml).

The other curve represents the kinetics of hydrolysis of gelatin under the same conditions and with the same ferment. We see that the two curves are quite similar. 45.5% of the polyalanine is decomposed by the ferment.

We made a quantitative determination of the alanine in the products of the cleavage of our polypeptide by an acid and by a ferment, using Furth's method [10],

which is based upon the oxidation of alanine, first by nitric acid to lactic acid, and then supplementarily by permanganate to acetaldehyde. This method is not without its disadvantages, but under our conditions (with no more highly complex amino acids present) it yields quite reliable results. The results of the Furth determination of alanine in both of the hydrolyzates were as follows:

Percentage of Alanine by the Furth Method

Hydrochloric acid hydrolyzate	Ferment hydrolyzate
35.3	44.9

Hence, both hydrolyzates contain a high percentage of free alanine, though a large part of the amino groups in the hydrolyzates do not pertain to alanine, but, evidently, to different peptides, di-, tri-, and higher polymers of alanine. In order to analyze these hydrolysis products of our polymer in detail, we resorted to adsorption analysis of amino acid mixtures, first proposed by Tsvet and elaborated by Tiselius [11], and recently developed in our laboratory as a simple micromethod. We modified Tiselius' method as follows: The unknown mixture of amino acids and peptides in aqueous solution, with a concentration no higher than 0.01 N [it also contains $MgCl_2$ owing to the neutralization of the HCl by $Mg(OH)_2$], is passed through a small column containing 0.5 g of Norite in a small Schott tube. Each 0.5 ml of solution passing through the charcoal was collected in a separate receiver, and then the refractive index of each solution was measured with the Haber-Loewe interferometer. Separate graduated curves were plotted for the adsorption of each of the components of the mixture, and then a curve was plotted for the mixture as a whole. This yields curves with marked steps. The adsorptive capacity with respect to alanine and its dipeptide (alanyl-alanine) is so different that the steps along the mixture curve can be readily identified as belonging to one component or another. The adsorption curve plotted for the acid hydrolyzate of our polypeptide is shown in Fig. 2. We see that alanine is certainly present in the mixture under analysis, and we may estimate it as 35% (by the difference between the ordinates for the first and second step), which is in good agreement with the Furth value found by us. Moreover, the dimer and $MgCl_2$ are likewise present. The first step on the curve denotes $MgCl_2$, the second one alanine, and the third one the dipeptide.

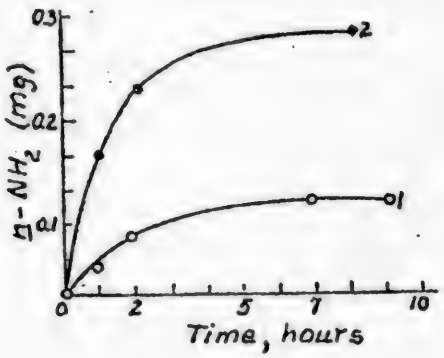


Fig. 1. Curves of the hydrolysis of gelatine and polyactamide under the action of a ferment.

1 - Polylactamide; 2 - Gelatine.

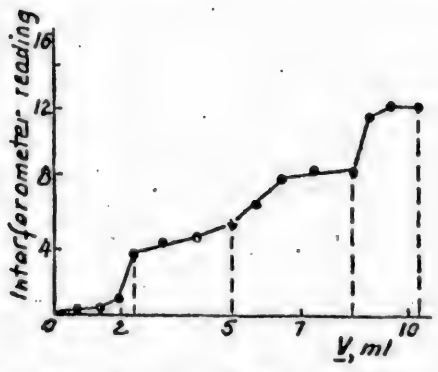


Fig. 2. Curve of the adsorption analysis of the hydrolysis product of polylactamide.

The Tiselius method provides us with independent confirmation of the fact that the products of the hydrolysis of the polypeptide contain a high percentage of alanine.

To understand the reason why our polypeptide is so easily attacked by the ferment, it was important to know whether it is a racemic product or close to the natural

polymer, containing only the l configuration of the amino acid. To ascertain this we measured the specific rotating power of the initial lactamide in a polarimeter. It proved to be [α] = 19.7 (in a pure configuration [α] = 22.2), i.e., the initial amide corresponded to 89% of the natural l-configuration of the alanine group, into which it was transformed during the ensuing polycondensation.

The polypeptides we have synthesized are readily acted upon by microflora, for which they evidently are a fully natural nutrient medium.

Measurement of the molecular weight of our polypeptides is extremely important. We have not yet been able to do so by a completely irreproachable method. A preliminary estimate, based on the viscosity of the alcoholic solution (according to Staudinger), gives the value of the molecular weight as 5000-6000, i.e., a polymerization stage of the order of 100. We are now engaged in measuring the molecular weight of thepolymers by diffusion methods, and shall make a special report on our results.

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Received July 21, 1948.

SYNTHESIS OF d,l-2,5-DIHYDROXYPHENYLALANINE FROM PHENOLS AND AROMATIC HYDROXYALDEHYDES

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2,5-Dihydroxyphenyalanine is of considerable biochemical interest as a possible intermediate product in the decomposition of aromatic amino acids in the animal organism. It is supposed that it is formed in the oxidation of tyrosine [1], later being either converted into homogentisic acid [2], or oxyhydroquinone [3], or undergoing oxidative decomposition of the aromatic ring after its oxidation to p-quinonealanine, in accordance with A.E.Braunshtein's hypothesis [4], which is most probable. He was unable to solve the problem of the role of 2,5-dihydroxyphenylalanine in the metabolism of the aromatic amino acids because of his lacking a satisfactory method for its synthesis. The difficulties involved in the synthesis of 2,5-dihydroxyphenylalanine are due to the ease with which it is oxidized, the formation of dark pigments (alcaptone bodies), and the possibility of cyclization (giving rise to compounds of the type of benzamino-umbelliferone [5]), as is well known in the case of the intermediate products of syntheses of substituted aromatic amino acids with an OH group in ortho position to the side chain [6].

The first and, up to the present time, the sole* method for the synthesis of 2,5-dihydroxyphenylalanine, by the Sasaki method [7], via 2,5-dimethoxybenzaldiketopiperazine with a yield of slightly more than 1% in terms of the initial salicylaldehyde (the synthesis described by Hirai [8]), cannot be considered satisfactory. Under the same conditions, the 2,4- [9] and 3,4- [10] dihydroxy derivatives of phenylalanine are synthesized (from the respective aldehydes) with much higher yields. Although the Hirai synthesis made it possible to cleave the diketopiperazine ring, reduce the double bonds, and remove the protective groups in one operation, it is accompanied by extremely high losses; that they could not be eliminated was confirmed by repetition of the synthesis, resulting in a yield of some 0.8% of the theoretical (based on salicylaldehyde).

Our research has shown that 2,5-dihydroxyphenylalanine can by synthesized much more easily via derivatives of 5-keto-hydro-oxazole, which is smoothly synthesized, with good yields, by condensing hippuric acid with 2,5-dihydroxybenzaldehyde, with free or, even better, with fully or partially methylated OH groups, by Erlenmeyer's "azlactone" method, followed by cleavage of the oxazole ring and reduction with hydroiodic acid. We have worked out three new ways of synthesizing 2,5-dihydroxyphenylalanine, using gentisinaldehyde, 2,5-dimethoxybenzaldehyde, and 2-hydroxy-5-methoxybenzaldehyde, respectively.

As we know, the compounds known as azlactones [12] and synthesized from aromatic aldehydes and benzoyl- [13,14] or acetylglycine [15], are frequently synthesized,

*At the end of 1947 there appeared Neugebauer's statement that he had evolved and would publish a better method for synthesizing 2,5-dihydroxyphenylalanine, but up to the present time no report on this subject has appeared in the literature, as far as we know.

chiefly to produce alpha amino acids with various substituents attached to the aromatic ring.

The dihydro-oxazole ring is usually cleaved by heating with alkali solutions [17] or by boiling for a short time with an alcoholic solution of HCl [18], followed by reduction of the substituted α-benzoyl-(acetyl)-aminocinnamic acids by sodium amalgam, hydroiodic acid, or catalytic hydrogenation. The optimum conditions differ widely for synthesis of the various amino acids, depending upon the structure of the cyclic ring. Thus, the excess of sodium amalgam employed in hydrogenating amino cinnamic acids varies from 10% [19] to 850% [20] of the theoretical in different syntheses. Catalytic reduction lasts as long as 24 days.

The method developed by Lamb and Robson [21], who synthesized phenylalanine and tyrosine with good yields by boiling the respective azlactones with HI and red phosphorus in acetic acid, is apparently best.

Thanks to the use of this operation in our syntheses and to the development of an improved method for isolating and purifying 2,5-dihydroxyphenylalanine, the overall yield in our experiments depended principally upon the efficiency with which the aromatic aldehydes were synthesized. Use of Adams' zinc-cyanide method [22] enabled us, starting with hydroquinone, to synthesize 2,5-dimethoxybenzaldehyde with good yields, and from the latter d,l-2,5-dihydroxyphenylalanine with an overall yield of 37.6% of the theoretical, in terms of hydroquinone.

The use of 2-hydroxy-5-methoxybenzaldehyde, synthesized by our modification of a new method of synthesizing aromatic hydroxyaldehydes [23], greatly simplified and facilitated the synthesis of 2,5-dihydroxyphenylalanine, even though it produced a somewhat lower yield of the end product. It is now possible to synthesize the latter in adequate quantities from easily available reagents. The time consumed is much less than that required in the bulky and not entirely safe operations of the zinc-cyanide method or the persulfate method (for synthesizing gentisinaldehyde).

EXPERIMENTAL

1. Synthesis of the Aldehydes

I,a. Gentisinaldehyde (2,5-dihydroxybenzaldehyde) was synthesized by the Neugebauer and Flatov method [24], involving the oxidation of salicylaldehyde (62 g) by potassium persulfate in a NaOH solution, followed by decomposition of the sulfuric mono ether of gentisinaldehyde by heating it to 70° with concentrated HCl (1.19). After extraction of the ether, and isolation and recrystallization from benzene, the product freed from the benzene of crystallization by drying at 50° weighed 16 g; the yield was 22.8% of the theoretical; m.p. 99° (Tiemann gives the m.p. as 99° [25].

I-b. We prepared 2,5-dimethoxybenzaldehyde by means of the Adams and Levine [22] zinc-cyanide method, which is a modification of the Hatterman syntheses of aromatic aldehydes; this method has been described by Gulland [26] as employed in the synthesis of 2-methoxy-5-ethylbenzaldehyde. The 1,4-dimethoxybenzene required in our synthesis was prepared by methylating hydroquinone dissolved in NaOH with methyl p-toluenesulfonate and was purified by steam distillation or recrystallization from alcohol. The yield was 95% of the theoretical in terms of hydroquinone.

100 g of 59% zinc cyanide (0.5 mol) is placed in a three-necked 1000-ml flask fitted with a mechanical stirrer and a mercury seal, and a solution of 35 g (0.25 mol) of hydroquinone dimethyl ether in 400 ml of chemically pure anhydrous benzene was added. A current of anhydrous HCl was passed through the mixture for 24 hours, fairly strongly at first, with rapid stirring. Then 55 g of anhydrous $AlCl_3$ was added and stirring with hydrogen-chloride treatment was continued for another 12

hours, the flask being warmed with water at about 40°. One day later the benzene layer is decanted, a solution of 34 ml of concentrated HCl (1.185) in 150 ml of water is added to the chilled residue, and after the salts dissolve, the whole is heated to 100° to decompose the intermediate imide hydrochloride. The aldehyde is driven off by steam. The crystals are drawn off from the aqueous distillate, and the latter is exhaustively extracted with ether (test with 2,4-dinitrophenylhydrazine). The ether (and the small amount of benzene driven over with the steam) are driven off from the extract, and after the dry residue is combined with the bulk of the aldehyde, it is purified via the bisulfite derivative to remove any possible traces of p-dimethoxybenzene. The aldehyde recovered by decomposing the bisulfite derivative is recrystallized from alcohol and water.

In the foregoing synthesis we employed 59% zinc cyanide, prepared by mixing 360 ml of a solution of zinc chloride (340 g of $ZnCl_2$; 2.49 mol) in 50% alcohol with a solution of 162 g of 95% KCN (2.44 mol) in 250 ml of water. Using potassium cyanide, we could not get a higher percentage of zinc cyanide, though a preparation containing 90% of the theoretical yield of $Zn(CN)_2$ is obtained from NaCN that has been freed from the carbonate by a preliminary treatment with magnesium chloride [22]. The pure product weighed 13.22 g after desiccation of the 2,5-dimethoxybenzaldehyde in a vacuum exsiccator over $CaCl_2$; the yield was 31.8% of the theoretical. M.p. 51° (Tiemann [25]: 51°). The use of 90% zinc cyanide in the synthesis of 2,5-dimethoxybenzaldehyde by the method described above raises the yield to 65% of the theoretical (Gulland [18], without describing the synthesis of this aldehyde, mentions the possibility of synthesizing it with a yield as high as 70%).

I-c. We synthesized 2-hydroxy-5-methoxybenzaldehyde by a slight modification of the method proposed by Duff [23] for the synthesis of some substituted p-hydroxybenzaldehydes. A mixture of 150 g of glycerol and 35 g of boric acid is heated in an evenly warmed 400-ml porcelain beaker fitted with a stirrer extending nearly to the bottom and a thermometer, the temperature being gradually raised to 170°. The mixture is kept at this temperature for half an hour, after which 20 g of hexamethylenetetramine, carefully triturated with 20 g of hydroquinone monomethyl ether recrystallized from benzine, is added in batches as rapidly as possible, but avoiding any foaming (periodically stopping the stirring and the heating). The temperature within the beaker is kept within 160-180° while this mixture is being added. After the mixture has been cooled to 110°, a hot solution of 30 ml of concentrated H_2SO_4 in 100 ml of water is added. The solution is transferred to a distilling apparatus and the aldehyde is driven off with steam. The end point of distillation is determined by the disappearance of the red color in a sample of the distillate mixed with 2,4-dinitrophenylhydrazine. The yellow precipitate due to formaldehyde persists in this sample for a long time. The distillate is extracted with ether, and the extract washed with anhydrous Na_2SO_4; the ether is driven off, and the remaining amber-colored oil is carefully desiccated in vacuum. The aldehyde weighs 6.8 g (27.7% of the theoretical). The product exhibits typical reactions: it turns blue-green with $FeCl_3$ and an intense yellow with alkalies; it crystallizes at a temperature below 4° [27]. The aldehyde is fully suitable for subsequent operations without any further purification.

In Duff's original method [23], described for other aldehydes, he recommends the successive, though separate, addition of hexamethylenetetramine followed by phenol to the boric acid – glycerol mixture. Using this recipe, we were unable to synthesize 2-hydroxy-5-methoxybenzaldehyde, but we did isolate a substance of unknown structure that crystallized as greenish lamellae at 15-20° and was useless for our needs.

II. Synthesis of Derivatives of Dihydro-oxazole

II.a. 5-Keto-2-phenyl-4-(2',5'-diacetoxybenzylidene)-4,5-dihydro-oxazole.

13.8 g (0.10 mol) of gentisinaldehyde (I-a) is triturated with 18 g (0.10 mol) of hippuric acid, and 12 g (0.146 mol) of finely pulverized, freshly fused, anhydrous sodium acetate is added; the whole is well mixed in a mortar and transferred to a 200-ml Jena-glass round-bottomed flask, 44.2 ml (47.8 g; 0.47 mol) of acetic anhydride is added, and the mixture is heated for about 1 hour over a boiling water bath. Some 15-20 minutes after the mixture fuses a yellow crystalline product usually settles out. The flask contents are cooled and then set aside to stand for 24 hours, the product is mixed with hot water (200 ml), drawn off, washed with 100 ml of water, triturated with ether (100 ml), again drawn off and washed with 100 ml of alcohol, and then with 100 ml of ether. The weight is 19.6 g (53.7% of the theoretical); m.p. 189.5-190°; m.p. is 191° after recrystallization from glacial acetic acid (according to Neugebauer [24] the yield is 48.4% of the theoretical and the m.p. is 190°). The substance is fairly readily soluble in pyridine and chloroform; it is less soluble in other organic solvents.

II-b. 5-Keto-2-phenyl-4-(2',5'-dimethoxybenzylidene)-4,5-dihydro-oxazole. 5 g (0.03 mol) of 2,5-dimethoxybenzaldehyde (IB) is triturated with 6 g (0.034 mol) of hippuric acid and 6 g (0.073 mol) of freshly fused sodium acetate; 10 g (0.1 mol) of acetic anhydride is added, and the whole is treated as set forth above. The crystalline product weighs 8.7 g (93.5% of the theoretical) after being washed w th water, alcohd, and ether; m.p. = 170°. Recrystallization of one gram of the product from 200 ml of boiling 96% alcohol yielded 0.94 g of beautiful orange needles with a m.p. of 171.5° (Gulland [18] gives the yield as 75% of the theoretical and the m.p. as 170-172°).

II-c. 5-Keto-2-phenyl-4-(2'-acetoxy-5'-methoxybenzylidene)-4,5-dihydro-oxazole. 11.8 g (0.07 mol) of hippuric acid is triturated with 13 g (0.18 mol) of freshly fused anhydrous sodium acetate; the mixture is placed in a reaction vessel, 23 ml of acetic anhydride is added, the whole is stirred, 8.6 g of liquid 2-hydroxy-5-methoxy-benzaldehyde (I-c) is added, the residue of the weighed batch of the aldehyde being transferred with the aid of 20 ml of acetic anhydride, and the whole mixture is heated for 1 hour over a boiling water bath. Soon after the mixture liquefies, large lustrous needles begin to settle out of the darkening liquid. They are cooled, mixed with 150 ml of boiling water the next day, drawn off on a porous No. 3 glass filter, and washed with another 150 ml of boiling water. The crystals are well mixed with 100 ml of alcohol, again drawn off, and washed with 50 ml of alcohol and then with 50 ml of ether. The crystals weigh 9.8 g (51.4% of the theoretical). Light orange needles; they fuse at 164-168°, but fusing sharply at 176.5-177° after recrystallization from hot 96% alcohol.

3.560 mg substance: 8.827 mg CO_2; 1.484 mg H_2O.
3.164 mg substance: 1.18 ml N_2 (23°, 743 mm).
Found %: C 67.66; H 4.66; N 4.20.
$C_{19}H_{15}O_5N$. Calculated %: C 67.65; H 4.48; N 4.15.

III. d,l-2,5-Dihydroxyphenylalanine

III-a. From 5-keto-2-phenyl-4-(2'acetoxy-5'-methoxy-benzylidene)-4,5-dihydro-oxazole (II-c). 9 g of the substance (II-c), 36 ml of chemically pure glacial acetic acid, 15 ml of acetic anhydride, 3.5 g of red phosphorus, and 36 ml of freshly distilled hydroiodic acid (sp. gr. 1.70) are placed in a 300-ml round-bottomed flask fitted with a ground-in reflux condenser. The whole is boiled for 3 hours and filtered out through a glass filter; the deposit of red phosphorus is washed with 50 ml of hot acetic acid, and the filtrate is diluted with 200 ml of water and concentrated at 30° in vacuum in a current of CO_2. It is not allowed to evaporate to dryness, 200 ml of water being added 4 times to effect more complete elimination of the free hydroiodic and acetic acids. Toward the end it is

evaporated to dryness, and the dark residue is desiccated in vacuum for 1 hour at 35° in a current of CO_2.

300 ml of anhydrous benzene is added, the mixture is boiled for a few minutes over a water bath, the benzene is decanted, and the operation is repeated with 200 ml of fresh anhydrous benzene. This removes the benzoic acid and a large part of the free iodine from the residue; it is then dried in vacuum to remove the traces of benzene, after which the substance is dissolved in 150 ml of water and 1 ml of glacial acetic acid. A 20% solution of lead acetate is added in batches until all the phosphates and iodides are precipitated out; after standing for a day at room temperature, the precipitate is removed in a centrifuge and washed with 3.5-4 volumes of water. The combined solution is chilled to 2-3°, filtered through a dense paper filter, and saturated with hydrogen sulfide; the PbS is removed, and the solution is evaporated to dryness in vacuum in a current of CO_2. 50 ml of absolute alcohol is added to the white, macrocrystalline residue to dissolve and remove any impurities, principally hydroquinonealanine hydroiodide, the crystals are well shaken up with alcohol and quickly transferred to a glass filter, suction is applied, and they are washed with 20 ml of absolute alcohol and 20 ml of anhydrous peroxide-free ether. The crystals weigh 5.10 g after desiccation over $CaCl_2$. They are recrystallized by dissolving this quantity in 120 ml of boiling water, passing some SO_2 through the solution, and setting it aside for a day in a refrigerator to crystallize. Large red rhombic prisims; weight 3.80 g. The mother liquor is reduced in vacuum to a volume of 30-40 ml, treated while boiling with a small amount of activated charcoal, filtered, and allowed to crystallize; this yields another 0.5 g of crystals that do not differ from the major batch. A total of 4.3 g of the recrystallized substance (74.90% of the theoretical) is recovered. The overall yield, based on hydroquinone monomethyl ether, is 10.7% of the theoretical (in terms of anhydrous 2,5-dihydroxyphenylalanine).

III b. From 5-keto-2-phenyl-4-(2',5'-dimethoxybenzylidene)-4,5-dihydro-oxazole (II-b). 2 g of the substance (II-b) is boiled for 4.5 hours with 6 ml of glacial acetic acid, 2 ml of acetic anhydride, 0.5 g of red phosphorus, and 8 ml of hydroiodic acid; the rest of the operation is the same as outlined under III-a. Driving off the water (after eliminating the PbS) yields 1.06 g of a dry crystalline residue. 0.5 g is dissolved in a mixture of 10 ml of 96% alcohol and 18 ml of water by heating it to boiling; the solution is treated with activated charcoal and filtered, the charcoal being washed with 3 ml of 30% alcohol. Some SO_2 is passed through the colorless filtrate, and 4 ml of absolute alcohol is added. Crystallization is brought about by placing the vessel in a freezing mixture (ice and salt) and rubbing; this caused a snow-white, finely crystalline precipitate of the amino acid to settle out. The deposit was filtered out after having been allowed to stand for a day in a refrigerator, and then washed with 4 ml of absolute alcohol and 20 ml of anhydrous peroxide-free ether. This yields 0.43 g of 2,5-dihydroxyphenylalanine; the overall yield, based on the hydroquinone, is 37.6% of the theoretical.

III c. From 5-keto-2-phenyl-4-(2',5'-diacetoxybenzylidene)-4,5-dihydro-oxazole (II-a). 3 g of the substance is boiled for 2.5 hours with 12 ml of glacial acetic acid, 4 ml of acetic anhydride, 1.2 g of red phosphorus, and 12 ml of hydroiodic acid (sp. gr. 1.70); further treatment was essentially the same as that in Experiment III-a. Recrystallized from water yielded 0.72 g of 2,5-dihydroxyphenylalanine (40.7% of the theoretical); the overall yield was 5.0% of the theoretical, based on salicylaldehyde.

The samples of a racemic compound synthesized by the methods described were authentic. They exhibit a collection of reaction for the hydroquinone group: they darken and blacken when shaken in air with solutions of NaOH and NH_3 (alcaptone

reaction); traces of $FeCl_3$ cause a green color, gradually changing to a dark color and forming a black precipitate upon standing; they are reduced by ammoniacal silver nitrate and mercury acetate in the cold; the Briggs reagent [sic] (phosphomolybdate and H_2SO_4) produces a characteristic green color, while pyridine produces a blue color (presence of an alpha amino acid group); and lead acetate does not precipitate the amino acid. It is not soluble in the usual organic solvents; water at 23° dissolves 0.6 g of the substance. The hydrochloride and the hydroiodide dissolve readily in water, acetic acid, and ethyl acetate. The free amino acid is precipitated by pyridine from solutions of its salts. The (dehydrated) substance fuses at 232-234° in a sealed tube; it crystallizes with one molecule of water, which it loses when heated with P_2O_5 for 4-5 hours to 100° at 30 mm.

0.3401 g substance: 0.0283 g H_2O.
Found %: H_2O 8.32.
Calculated %: H_2O: 8.37.

We analyzed a mixed sample of the substance, obtained from the three syntheses and dehydrated:

3.931 mg substance: 0.244 ml N_2 (22°, 750 mm).
3.843 mg substance: 7.711 mg CO_2; 1.937 mg H_2O.
Found %: N 7.09; C 54.76; H 5.64.
$C_9H_{11}O_4N$. Calculated %: N 7.10; C 54.81; H 5.62.

Other properties of d,l-2,5-dihydroxyphenylalanine and its derivatives, synthesized by us, as well as the ways of separating the optical isomers, will be described in a separate report.

SUMMARY

1. Three new methods of synthesizing d,l-2,5-dihydroxyphenylalanine via derivatives of 5-ketodihydro-oxazole, starting with salicylaldehyde, hydroquinone, and hydroquinone monomethyl ether, have been developed.

2. The most effective method of synthesizing hydroquinone-alanine proved to be via 2,5-dimethoxybenzaldehyde, synthesized by the zinc-cyanide method; the hydroquinone-alanine was synthesized with a yield of 37.6% of the theoretical in terms of hydroquinone by decomposing the dihydro-oxazole derivative prepared from it. The synthesis from hydroquinone monomethyl ether via 2-hydroxy-5-methoxybenzaldehyde gives a lower yield, but it merits preference because of the accessibility of the raw material and the simplicity of operations. The synthesis via gentisinaldehyde is least profitable.

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Received July 18, 1948.

ALKALOIDS OF COCCULUS LAURIFOLIUS D. C. I

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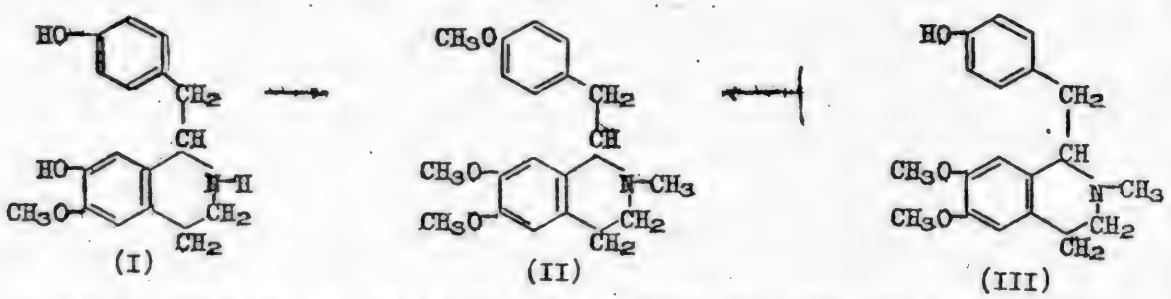
Cocculus laurifolius D.C. (fam. Minispermaceae) is an evergreen shrublike tree, the leaves of which are covered with a lustrous substance; externally they look like laurel leaves. It grows principally in southern China, India, and Japan, and is extensively employed in the folk medicine of the East.

The Chinese drug "Koshiu-uyaku" and the Japanese "Kamegome-jin" are the dried root of Cocculus laurifolius D.C.

Greshoff [1] isolated an amorphous alkaloid for the first time (1890) from the root and leaves of this tree and called it "coclaurine." Crystalline pure coclaurine, $C_{17}H_{19}NO_3$, was isolated by the Japanese chemists H. and T. Kondo [2] in 1925 from the leaves and trunk of this plant. The authors succeeded, by complicated methods, in establishing the structure of this alkaloid (I); their results were set forth in their fifth [2] and sixth reports [3] in 1930.



(I) (II) (III)

We isolated a new alkaloid, which we named armepavine, together with other bases, from Papaver armeniacum and P. floribundum [4]. After we had established the structure of armepavine itself (III), as well as methylarmepavine (II), we discovered that the latter's properties contradicted the properties of what H. and T. Kondo called trimethylcoclaurine, which evidently had to have a structure that was identical with that of our methylarmepavine (II). The properties specified by H. and T. Kondo for trimethylcoclaurine differ sharply, however, from the properties of methylarmepavine. In our previous report we pointed out the errors committed by the Japanese chemists H. and T. Kondo, which resulted in the discrepancy between their data and ours for the given substance (II) [5]. Commencing an investigation of this plant, we proposed to isolate coclaurine and methylate the hydroxyl group of the latter by diazomethane and the secondary nitrogen by formaldehyde and formic acid, and, by thus synthesizing trimethylcoclaurine, to furnish experimental proof of the objections we had raised in our previous report [5].

Moreover, H. and T. Kondo succeeded in isolating only one alkaloid from Cocculus laurifolius D.C., and as we are of the general opinion that there is no

such thing as a plant containing only one alkaloid throughout its period of development, we proposed to isolate another alkaloid, besides coclaurine, from the leaves of this tree. But exploration of the alkaloids isolated by us from the leaves of this plant indicated that it contains no coclaurine at all. Instead, we isolated two alkaloids: one of them phenolic, and the other nonphenolic, but both completely distinct from coclaurine. Coclaurine, for example, has the constitutional formula $C_{18}H_{13}(=N-)(OCH_3)(OH)_2$; the alkaloids we isolated have the formulas: $C_{18}H_{27}(=N-)(OCH_3)(OH)$ and $C_{18}H_{27}(=N-)(OCH_3)_2$, the nitrogen being tertiary in both instances, but not containing an N-methyl group. We shall deal with the other differences in the properties of these alkaloids below, but it is out of the question that the bases isolated by us are identical with coclaurine.

The leaves of Cocculus laurifolius D.C. examined by us were first received [6] in 1939, and then in 1945 from the city of Batumi, thanks to the kindness of the chief of the Acclimatization Section of the Batumi Subtropical Botanical Garden, P.M. Kibalchich, to whom we wish to express our sincere gratitude. Cocculus laurifolius D.C. was first brought to this garden from southern China in 1912 by Prof. Krasnov, the garden's founder. The Japanese also get the plant from there for their research and preparation of drugs. It is a fact that in the Cocculus laurifolius D.C. investigated by us, growing in the Batumi area since 1912 and gathered in 1939, two new alkaloids have been found instead of coclaurine, which this plant contains in its native soil. This demonstrates that a change in the soil and climatic conditions of growth of Cocculus laurifolius D.C. resulted in the formation of new alkaloids in this plant.

The alkaloids were isolated in the usual manner – by extraction with dichloroethane. The chilled sulfuric-acid solution of the bases was alkalinized with gaseous ammonia, after which all the alkaloids were extracted with ether. The percentage of alkaloids in the leaves of Cocculus laurifolius D.C. proved rather high, totaling 0.9% of the dry weight of the leaves, of which 0.75% represented a phenolic alkaloid and 0.15% constituted a nonphenolic alkaloid. It should be noted that these leaves were gathered in May (1939), whereas leaves gathered in August (1946) contained less than 0.7% of total alkaloids, but the ratio of the phenolic and nonphenolic alkaloids was practically unchanged. Unfortunately, we were unable to make a detailed study of the qualitative and quantitative changes in the alkaloids with the season of the year, in the leaves as well as in the other organs of this plant. But we do not doubt that qualitative and quantitative changes occur in this plant with the seasons of the year, notwithstanding the fact that Cocculus laurifolius D.C. is an evergreen. Apparently, the leaves contain a maximum quantity of total alkaloids during the spring, the period of intensive plant growth, the bark and the roots containing a maximum in the autumn and winter. A mixture of the nonphenolic bases constituted a thick brown oil, which is highly soluble in nearly all organic solvents, with the exception of petroleum ether. We were able to make the whole mass partially crystallize by triturating it with a small quantity of petroleum ether, but isolating the individual crystalline bases entailed very great difficulties. Only after a number of attempts were we finally able to isolate a single pure crystalline alkaloid, by constituting a crystalline hydriodate in ethyl acetate or acetone.

In general, our observations in a number of instances indicate that if an alkaloid yields a well-crystallizing iodomethylate, this alkaloid yields a well-crystallizing hydriodate, and vice versa, i.e., a well-crystallizing hydriodate gives a well-crystallizing iodomethylate. In this case, we were governed by this rule in obtaining a hydriodate from a mixture of bases that resisted the formation of crystalline salts.

The isolated crystalline alkaloid constituted about 70% of the mixture of nonphenolic bases. This substance crystallizes readily from petroleum ether and has

a m.p. of 86-87° and $[\alpha]_D$ + 250.90°. We found the empirical formula to be $C_{18}H_{23}NO_2$, based on an elementary analysis and a determination of the molecular weight.

As this alkaloid burns with difficulty, the foregoing composition was confirmed by combustion of the nitrate of the base. The alkaloid proved to differ from all those described in the literature up to now, and we gave it the name of "coculidine". The presence of two methoxy groups was established by the Viebeck method, no N-methyl group or active hydrogen (NH) being found, but the nitrogen was tertiary, and it immediately yielded a beautifully crystallizing iodomethylate. Thus, the formula for coculidine may be expanded as follows, as indicated above:

$$C_{18}H_{17}(=N-)(OCH_3)_2.$$

In the mother liquor (30%) left after the coculidine was isolated, there doubtless are other nonphenolic alkaloids still unrecovered in pure form, but owing to the small quantity of the mother liquor our endeavors to isolate them in the pure state were unsuccessful. We hope to be able to isolate at least one other base, in addition to coculidine, by accumulating more of the mother liquor. As for the phenolic portion (0.15%) of the total alkaloids, it was found that it consists almost entirely of a single alkaloid, which is obtained at once in crystalline form and recrystallizes very readily from acetone and alcohol, with a m.p. of 217-218° and $(\alpha)_D$ + 271.1°. This phenolic base yields salts that crystallize readily, the nitrate, the hydrochloride, and the iodomethylate. On the basis of elementary analysis of the base itself and of its nitrate, and determinations of the molecular weight and of the chlorine in the hydrochloride, we established its elementary composition as $C_{17}H_{21}NO_2$ and called the alkaloid "coculine". The presence of a single hydroxyl group was established by the Tserevitinov method; the phenolic properties of this group were established by the solubility of coculine in alkalies. A single methoxyl group was discovered by the Viebeck method; no methyl imide group was found, but the nitrogen was found to be tertiary. Hence the formula for coculine may be expanded as follows:

$$C_{16}H_{17}(=N-)(OCH_3)(OH).$$

As may be clearly seen from the expanded formulas for coculine and coculidine, they are both derivatives of the same fundamental ring $C_{16}H_{19}N$. This situation suggests that coculidine may be the monomethyl ester of coculine. In our further study of coculine we were able to confirm this experimentally; viz: by methylating coculine with diazomethane, we synthesized a crystalline base that was insoluble in alkalies, had a m.p. of 86-87°, and exhibited no depression of the melting point when mixed with a test sample of coculidine. Hence, the further study of the structure of the basic skeleton and the establishment of the position of the methoxyl groups in the two alkaloids boiled down to one.

The pharmacological investigation of coculine and coculidine has been commenced by Prof. M.D.Mashkovsky [7].

EXPERIMENTAL

Isolation of the Alkaloids

6 kg of air-dried, finely ground leaves of Cocculus laurifolius D.C. were wetted with 5% ammonia and percolated with dichloroethane (5 times) until the alkaloids were completely extracted. The dichloroethane solution was exhaustively extracted with 10% sulfuric acid. The sulfuric-acid extract was filtered, and then chilled with ice water and alkalinized with 25% ammonia in the presence of ether, the base being completely extracted by the ether. The ether extract was reduced to a volume of 1 liter. It was then treated with 100 ml of a 5% solution of sodium hydroxide (ether extract A), the alkaline solution was again washed with ether, and 100 ml of an aqueous alkaline solution was added to ether extract A, after which it was acidulated, while chilled, with 50% sulfuric acid and again alkalinized with 25% ammonia in the

presance of ether. After the ether extract had been removed, the alkaline solution was again extracted with ether several times. Driving off the ether from the combined extracts left 8 g (0.15%) of a crystalline phenolic base. After the ether had been driven off from the ether extract A, and the traces of water had been removed in a vacuum exsiccator, we obtained 45 g (0.75%) of a nonphenolic base as a thick brown oil. The total yield of alkaloids was 53 g (0.9% of the dry weight of leaves).

Separation and Purification of Nonphenolic Alkaloids

The mixture of nonphenolic alkaloids is insoluble in water, but readily soluble in nearly all the ordinary organic solvents. We were able to crystallize it by treating it with a small quantity of petroleum ether. But an attempt to purify the crystalline alkaloid (coculidine) by recrystallization (from petroleum ether and other organic solvents) failed, since we always recovered oily crystals contaminated with other bases.

45 g of the alkaloid mixture was dissolved in 35 ml of ethyl acetate or acetone, and strong hydriodic acid was added to the solution, chilled with ice, until it exhibited a weak acid reaction to litmus. This caused yellowish crystals of coculidine to settle out. The yield was 29 g. The mother liquor was evaporated in vacuum, and all the residue was converted into the free base. From the latter we recovered another 8 g of crystalline hydriodate that was identical with the 29 g of hydriodate. The third time we recovered 4 g. Thus, of the 45 g of total nonphenolic bases, 41 g of commercial coculidine hydriodate is recovered, though we are unable to isolate the individual pure base from the mother liquors by the method described. This mother liquor, 7 g of brown oil, requires further treatment.

Purifying coculidine hydriodate. 41 g of the crude coculidine hydriodate was dissolved in hot ethyl acetate, and the solution was treated with charcoal. When the filtered solution was cooled, white, thickened, acicular crystals of coculidine, with a m.p. of 105-110°, settled out. But if the temperature is gradually raised after fusion, the substance solidifies again at 110-120°, melting again at 173-175°. The m.p. is 174-175° after drying at 90-100° at 12-15 mm. The same crystals are produced by crystallization from water, losing water of crystallization at 110° and fusing again at 175°. Further recrystallization did not affect the melting point. Yield: 38 g.

0.3696 g substance: 0.0156 g H_2O (90°, 15 mm).
Found %: H_2O 4.22.
$C_{18}H_{23}O_2N \cdot HI \cdot H_2O$. Calculated %: H_2O 4.18.
0.1760 substance : 4.3 ml 0.1 N $AgNO_3$.
0.1345 substance: 3.3 ml 0.1 N $AgNO_3$.
Found % I 31.02, 30.34.
$C_{18}H_{23}O_2N \cdot HI$. Calculated%: I 30.75.

Coculidine

38 g of coculidine hydriodate was dissolved in 40 ml of water, and in the presence of 5 ml of petroleum ether 25% ammonia was added until the reaction was alkaline. The white crystalline base that settled out was filtered out by suction and washed with water. The base was extracted from the alkaline mother liquor with ether. The crystalline base that was left after the ether had been driven off was combined with the base that precipitated out of the ammonia solution. Total yield: 24 g. The finely crystalline base was recrystallized from petroleum ether; coculidine settled out of the chilled solution as colorless prisms with a m.p. of 86-87°. Coculidine is readily soluble in alcohol, chloroform, and ether, soluble with more difficulty in petroleum ether, and nearly insoluble in water.

0.1332 g substance: in 12 ml chloroform; l 1.005 dm.
α_D + 2.5°; $[\alpha_D]$ + 250.90°.
3.826 mg substance: 10.660 mg CO_2; 2.674 mg H_2O.
3.150 mg substance: 8.752 mg CO_2; 2.178 mg H_2O.
5.620 mg substance: 0.245 ml N_2 (22°, 743 mm).
5.955 mg substance: 0.258 ml N_2 (22°, 743 mm).
20.90 mg substance: 8.61 ml 0.1 N $Na_2S_2O_3$.
16.25 mg substance: 6.69 ml 0.1 N $Na_2S_2O_3$.
0.1162 g substance: 4.1 ml 0.1 N HCl.
0.7319 g substance: 17.54 g C_6H_6: Δt 0.753°.
0.5976 g substance: 17.55 g C_6H_6: Δt 0.617°.
Found %: C 75.99, 75.77; H 7.82, 7.74; N 4.93, 4.90; OCH_3 21.25, 21.14; M 283.41, 283.7, 282.5; no NCH_3 or OH groups were found.
$C_{18}H_{23}O_2N$. Calculated %: C 75.79; H 8.13; N 4.91; OCH_3 21.75; M 285.

Coculidine nitrate. Strong nitric acid was added drop by drop to a saturated solution of the base in ethyl acetate or acetone until the solution was weakly acid. Chilling caused the finely crystalline coculidine nitrate, with a m.p. of 131.5-132.5° to settle out; the melting point was raised to 137-138° after recrystallization from acetone. Like the hydroiodate, the nitrate may be successfully used in purifying coculidine.

4.454 mg substance: 10.153 mg CO_2; 2.714 mg H_2O.
3.040 mg substance: 6.920 mg CO_2; 1.884 mg H_2O.
5.155 mg substance: 0.363 ml N_2 (22°, 743 mm).
5.250 mg substance: 0.373 ml N_2 (22°, 743 mm).
Found %: C 62.17, 62.08; H 6.82, 6.93; N 7.97, 8.04.
$C_{18}H_{23}O_2N \cdot HNO_3$. Calculated %: C 62.05; H 6.94; N 8.04.

Coculidine iodomethylate. 0.3 g of coculidine was dissolved in 3 ml of methanol, and 0.6 ml of methyl iodide was added to the solution. The reaction was complete after 40 minutes of boiling, as was shown by the disappearance of the solution's alkaline reaction to litmus. Then the solution was reduced to one-third of its initial volume. This caused coculidine iodomethylate to settle out as transparent, prismatic crystals. After chilling with ice, the crystals were filtered out with suction and washed with acetone; m.p. = 238-239°. The melting point of the 0.35 g of iodomethylate recovered did not change with further recrystallization from alcohol or acetone.

0.1764 g substance: 4.15 ml 0.1 N $AgNO_3$.
0.1294 g substance: 3.05 ml 0.1 N $AgNO_3$.
Found %: I 29.87, 29.93.
$C_{18}H_{23}O_2NCH_3I$. Calculated %: I 29.74.

Phenol Base (Coculine)

8 g of crystalline crude coculine, with a m.p. of 215-216.5°, was purified by recrystallization from acetone. One recrystallization yielded crystals in the shape of well-formed transparent prisms, with a m.p. of 217-218°. This melting point did not change with further recrystallization from acetone or alcohol. Coculine yields a well-crystallized hydrochloride; the base recovered from the latter also has a m.p. of 217-218°. The yield of pure alkaloid was 5.8 g (0.1% of the weight of the dry leaves). The mother liquor is a thick brown mass.

Our efforts to obtain a pure base and a salt from the mother liquor failed because of the small quantity available. Coculine is readily soluble in chloroform, less so in alcohol, acetone, and ether, and almost insoluble in water. Notwithstanding its strongly marked phenolic character, it may be kept for years in air

as the free base.

0.0818 g substance: 10 ml methanol: 1 0.947 dm; α_D + 2.1; $[\alpha]_D$ = + 271.1°.
4.030 mg substance: 11.150 mg CO_2; 2.935 mg H_2O.
3.752 mg substance: 10.3[illegible] mg CO_2; 2.670 mg H_2O.
0.1706 g substance: 8.7 ml N_2 (28°, 693 mm).
0.1692 g substance: 8.1 ml N_2 (24°, 704 mm).
17.70 mg substance: 3.94 ml 0.1 N $Na_2S_2O_3$.
18.49 mg substance: 4.12 ml 0.1 N $Na_2S_2O_3$.
14.50 mg substance: 1.20 ml CH_4 (0°, 760 mm).
17.470 mg substance: 1.39 ml CH_4 (0°, 760 mm).
0.1130 g substance: 4.2 ml 0.1 N HCl.
Found %: C 75.46, 75.[illegible]; H 8.15, 7.9[illegible]; N 5.27, 5.09; OCH_3 11.51, 11.5[illegible]; Cl [illegible]; M 269.5.
$C_{17}H_{21}O_2N$. Calculated %. C 75.27; H 7.80; N 5.19; OCH_3 11.44; OH 6.27; M 271.34.

Coculine nitrate. 1 g of coculine was dissolved, with heating, in 10 ml of absolute alcohol, and, while the solution was rapidly chilled with ice, strong nitric acid was added a drop at a time until the solution was weakly acid. This caused crystalline coculine nitrate, with a m.p. of 196-197°, to settle out. Neither the melting point nor the weight was affected by recrystallization from alcohol or by drying in vacuum.

4.090 mg substance: 9.177 mg CO_2; 2.360 mg H_2O.
3.025 mg substance: 6.776 mg CO_2; 1.774 mg H_2O.
3.970 mg substance: 0.296 ml N_2 (22°, 737 mm).
4.065 mg substance: 0.301 ml N_2 (22°, 737 mm).
Found %: C 61.19, 61.09; H 6.46, 6.56; N 8.37, 8.31.
$C_{17}H_{21}O_2N \cdot HNO_3$. Calculated %: C 61.06; H 6.63; N 8.37.

Coculine hydrochloride. A strong alcoholic solution of hydrochloric acid was added to a saturated alcoholic solution of the base, causing a snow-white finely crystalline precipitate of coculine hydrochloride, with a m.p. of 106-110°, to settle out. Raising the temperature gradually after fusion causes the substance to recrystallize at 120-130° and to fuse again at 222-223°. After desiccation, the substance fuses at once at 222-223°.

0.2020 g substance: 6.21 ml 0.1 N $AgNO_3$.
0.1812 g substance: 0.0092 g H_2O (100°, 12 mm).
Found %: Cl 10.90; H_2O 5.08.
$C_{17}H_{21}O_2N \cdot HCl \cdot H_2O$. Calculated %: Cl 10.91; H_2O 5.5.

Methylation of Coculine by Diazomethane (O-Methylcoculine)

1 g of coculine (m.p. 217-218°) was dissolved in 10 ml of anhydrous methanol, and an ether solution of diazomethane, prepared from 7 g of nitrosomethylurea, was added to the solution. The solution was allowed to stand for 5 days. Then the excess diazomethane was driven off, and the remaining ether solution was washed with 5% NaOH and with water. After desiccating the ether solution over anhydrous potash, the solvent was driven off. The residual thick, oily substance crystallized completely after a small amount of petroleum ether was added. Recrystallization from petroleum ether yielded the crystals as prisms with a m.p. of 86-87°. A test sample mixed with coculidine exhibited no depression of the melting point. For o-methylcoculine we found $[\alpha]_D$ + 249.6°; we synthesized the iodomethylate with a m.p. of 237-238°. A test sample mixed with coculidine iodomethylate exhibited no lowering of the melting point.

SUMMARY

1. Cocculus laurifolius D.C., brought from South China to the Batumi region in 1912 and investigated by us in 1939, does not contain the principal alkaloid coclaurin, which is characteristic of this plant in its native land. Instead, new alkaloids have appeared in this plant: coculine, $C_{17}H_{21}NO_2$, of phenolic character, and nonphenolic coculidine, $C_{18}H_{23}NO_2$. The phenol portion of an alkaloid mixture obtained during the plant's growth period under investigation consists nearly entirely of coculine, while the nonphenolic portion consists of coculidine (70%) and other alkaloids, which we have as yet been unable to isolate in the pure state.

2. Quantitative determination of the functional groups enables the formulas of the two alkaloids to be analyzed as follows: coculine – $C_{16}H_{17}(=N-)(OCH_3)(OH)$, and coculidine – $C_{16}H_{17}(=N-)(OCH_3)_2$.

3. Coculidine is the monomethyl ester of coculine. Both alkaloids are derivatives of the basic skeleton $C_{16}H_{19}N$.

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Received July 23, 1948.

DERIVATIVES OF ACETYLENE

106. RESEARCH ON HETEROCYCLIC COMPOUNDS

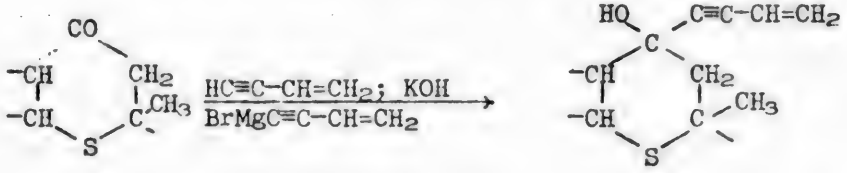
X CONDENSATION OF VINYLACETYLENE WITH TETRAHYDRO-γ-THIOPYRONES. SYNTHESIS OF 4-VINYLETHYNYLTETRAHYDROTHIOPYRAN-4-OLS

I. N. Nazarov, A. I. Kuznetsova and I. A. Gurvich

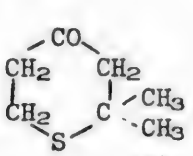
In our preceding report we described the synthesis of tetrahydrothiopyranols of the acetylene series by condensing acetylene with tetrahydro-γ-thiopyrones in the presence of powdered potassium hydroxide [1].

We were also interested in condensing vinylacetylene with tetrahydro-γ-thiopyrones in order to synthesize various tetrahydro-γ-thiopyranols of the vinylacetylene series, which have remained wholly inaccessible and unexplored up to the present time.

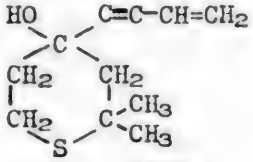
As might have been expected, this reaction is fairly smooth, yielding vinylacetylenic thiopyranols in accordance with the following diagram:



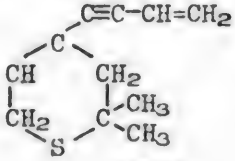
The condensation of 2,2-dimethyltetrahydro-1-thiopyran-4-one (I) with vinyl acetylene in the presence of powdered potassium hydroxide yields about 50% of 2,2-dimethyl-4-vinylethynyltetrahydrothiopyran-4-ol (II), whereas this thiopyranol is synthesized with a yield of some 85% by reacting vinylacetylenemagnesium bromide with the thiopyranone (I):



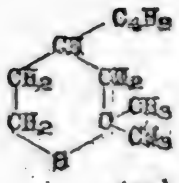
(I)



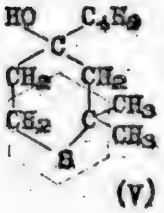
(II)



(III)



(IV)



(V)

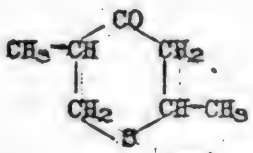
Dehydration of the thiopyranol (II) by potassium bisulfate yielded 2,2-dimethyl-4-vinylethynyl-$\Delta^{4,5}$-dihydrothiopyran (III). The location of the double bond in the ring was established by analogy with the product of dehydration of 2,2-dimethyl-4-vinylethynyltetrahydropyran-4-ol, in which its position had been established earlier [2].

When the vinylacetylenic dihydrothiopyran (III) was hydrogenated in the presence of a palladium catalyst*, four molecules of hydrogen were absorbed and 2,2-dimethyl-4-butyltetrahydrothiopyran (IV) was synthesized.

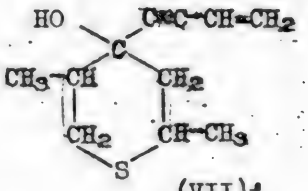
Condensation of the thiopyrone (I) with butylmagnesium chloride yielded 2,2-dimethyl-4-butyltetrahydrothiopyran-4-ol (V).

Hydrogenation of the vinylacetylenic thiopyranol (II) by hydrogen with a palladium catalyst is not complete, however, and the wholly pure thiopyranol (V) cannot be recovered in this instance.

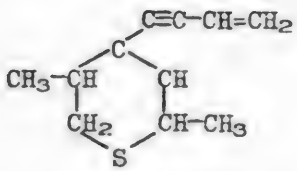
The action of vinylacetylenemagnesium bromide on the thiopyrone (VI) (an isomer with a m.p. of 71°) produces a good yield of 2,5-dimethyl-4-vinylethynyltetrahydrothiopyran-4-ol (VII):



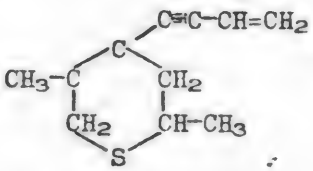
(VI)



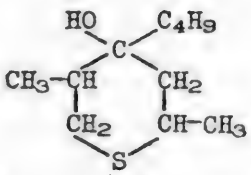
(VII)



(VIII)



(IX)



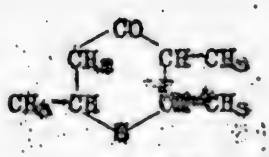
(X)

When the thiopyranol (VII) is heated with p-tcluenesulfonic acid, water is detached and 2,5-dimethyl-4-vinylethynyldihydrothiopyran (VIII) or (IX) is formed.

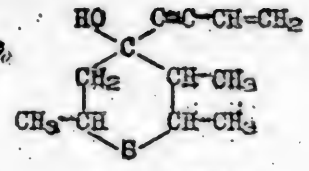
The action of butylmagnesium chloride upon the thiopyrone (VI) yields 2,5-dimethyl-4-butyltetrahydrothiopyran-4-ol (X).

Similarly, the action of vinylacetylenemagnesium bromide upon the thiopyrone (XI) yielded 2,3,6-trimethyl-4-vinylethynyltetrahydrothiopyran-4-ol (XII), dehydration of which yielded the dienyne (XIII) or (XIV):

* In the presence of a Pt catalyst vinylethynyldihydrothiopyran (III) is not hydrogenated at all.



(XII)



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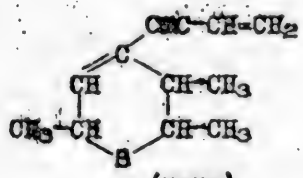

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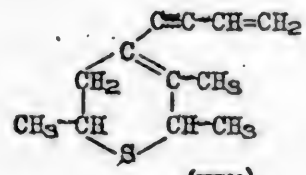
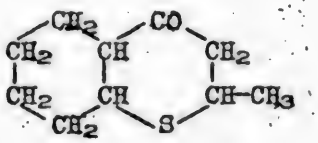


The action of vinylacetylenemagneisum bromide and butyl magnesium chloride upon 2-methylhexahydrothiochroman-4-one (XV) (an isomer with a m.p. of 77-78°) synthesized 2-methyl-4-vinylethynylhexahydrothiochroman-4-ol (XVI) and 2-methyl-4-butylhexahydrothiochroman-4-ol (XVII), respectively:.



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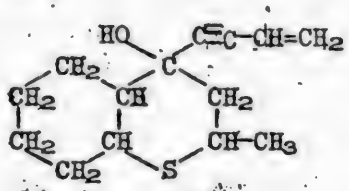

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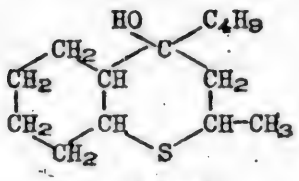
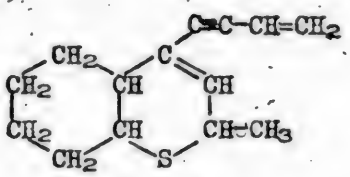
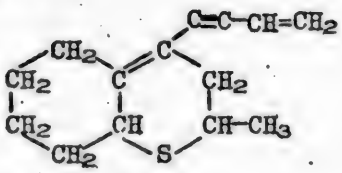


(XVII)



(XVIII)



(XIX)

Dehydration of the vinylacetylenic thiochromanol (XVI) in the presence of p-toluenesulfonic acid yielded the dienynes (XVIII) or (XIX).

We endeavored to effect the hydration and cyclization of the dienynes of the thiopyran series [the dienyne (III), in particular] into the corresponding dienones (vinyl allyl ketones) and cyclopentenones, as may be done extremely easily with aliphatic and alicyclic dienynes. All our efforts in this field remained fruitless, however, as the dienynes of the thiopyran series are very hard to hydrate, tarring readily when this is attempted.

Before the appearance of our paper only a few thiopyranols with aromatic substituents had been described in the literature, to wit: 4-phenyltetrahydrothiopyran-4-ol, 4-benzyltetrahydrothiopyran-4-ol [3], and 4-methyl-2,6-diphenyltetrahydrothiopyran-4-ol [4].

EXPERIMENTAL

The tetrahydro-Y- thiopyrones used for condensations with vinylacetylene were prepared by the action of hydrogen sulfide upon vinyl allyl ketones and β,β-dimethyldivinyl ketone, as described in our previous reports [5]

2,2-Dimethyl-4-vinylethynyltetrahydrothiopyran-4-ol.

a) 20 ml of absolute ether was added to 15 g of powdered potassium hydroxide, and a solution of 20 g of vinylacetylene and 36 g of 2,2-dimethyltetrahydro-1-thiopyran-4-one (I) in 60 ml of absolute ether was gradually added with vigorous stirring and chilling with ice water.

The reaction mass was stirred for 8 hours at 0° and for 4 hours at room temperature. The alkali was washed out with 20 ml of water, and the ether solution was neutralized with 5% hydrochloric acid and desiccated with sodium sulfate.

Distillation yielded 22 g of 2,2-dimethyl-4-vinylethynyltetrahydrothiopyran--4-ol (II) as a glycerol-like liquid:

B.p. 131-132° at 8 mm; n_D^{20} 1.5458; d_4^{20} 1.0521.
MR found 58.97; calculated 57.61.

8.427 mg substance: 10.125 mg $BaSO_4$.
15.765 mg substance: 18.660 mg $BaSO_4$.
Found %: S 16.50, 16.27.
$C_{11}H_{18}OS$. Calculated %: S 16.32.
0.1608 g substance: 14.7 g benzene: Δt 0.273°.
0.1547 g substance: 14.7 g benzene: Δt 0.262°.
Found: M 205.56, 206.03.
$C_{11}H_{18}OS$. Calculated: M 196.

b) A solution of 14 g of vinylacetylene in 100 ml of ether was gradually added to a solution of ethylmagnesium bromide, prepared from 7 g of magnesium, 35 g of ethyl bromide, and 150 ml of ether. The reaction was brought to an end by heating the ether solution over a water bath for an hour. 30 g of the thiopyrone (I), dissolved in 25 ml of ether, was gradually added to the chilled reagent. The reaction mixture was stirred for 5 hours at room temperature, and then was heated over a water bath for an hour. While chilled with ice water the product was hydrolyzed with 17% hydrochloric acid (200 ml), extracted with ether, washed with a soda solution, desiccated with sodium sulfate, and distilled. This yielded 33 g of the thiopyranol (II), with a b.p. of 122-123° at 4 mm; n_D^{15} 1.5458. The yield was 82% of the theoretical.

2,2-Dimethyl-4-vinylethynyl-$\Delta^{4,5}$-dihydrothiopyran.

12 g of the thiopyranol (II) was heated in a 12-mm vacuum in the presence of 4 g of finely ground potassium bisulfate and a small quantity of pyrogallol. At 175° water began to be given off, and 8 g of a substance with a m.p. of 124-128° (12 mm) was driven off. The product was extracted with ether, dried with magnesium sulfate, and distilled. This yielded 2,2-dimethyl-4-vinylethynyl-$\Delta^{4,5}$-dihydrothiopyran (III) as a mobile yellow liquid with a disagreeable odor:

B.p. 110.5-111.5° at 6 mm; n_D^{20} 1.5656; d_4^{20} 0.9917.
MR found 58.61; calculated 55.83.

6.607 mg substance: 17.857 mg CO_2; 4.703 mg H_2O.
3.708 mg substance: 10.185 mg CO_2; 2.750 mg H_2O.
Found %: C 73.76, 73.53; H 7.97, 8.03.
$C_{11}H_{14}S$. Calculated %: C 74.10; H 7.85.
4.424 mg substance: 5.721 mg $BaSO_4$.
4.920 mg substance: 6.337 mg $BaSO_4$.
Found %: S 17.76, 17.69.
$C_{11}H_{14}S$. Calculated %: S 17.97.

2,2-Dimethyl-4-butyltetrahydrothiopyran.

5.5 g of the vinylacetylenic dihydrothiopyran (III), dissolved in 50 ml of

alcohol, was hydrogenated with hydrogen in the presence of 1 g of a palladium catalyst deposited upon calcium carbonate. The catalyst was added in three batches. Hydrogenation lasted 12 hours until no more hydrogen was absorbed. A total of 2.5 liters of hydrogen was absorbed, instead of the 2.7 liters required theoretically.

The usual treatment yielded 3.5 g of 2,2-dimethyl-4-butyltetrahydrothiopyran (IV), a colorless liquid:

B.p. 110-110.5° at 12 mm: n_D^{20} 1.4885; d_4^{20} 0.9167.
Found MR 58.54; calculated, 58.76.

3.034 mg substance: 3.775 mg $BaSO_4$.
4.400 mg substance: 5.443 mg $BaSO_4$.
Found %: S 17.09, 16.99.
$C_{11}H_{22}S$. Calculated %: S 17.20.

2,2-Dimethyl-4-butyltetrahydrothiopyran-4-ol.

14 g of the thiopyranone (I), dissolved in 20 ml of ether, was gradually added to a solution of butylmagnesium chloride prepared from 2.5 g of magnesium, 11.5 g of butyl chloride, and 25 ml of ether. The reaction mixture was stirred for 1 hour at room temperature and then it was boiled for 2 hours. The solution, chilled with ice water, was hydrolyzed with 20% acetic acid and extracted with ether. The ether solution was washed with a soda solution, dried with sodium sulfate, and distilled in vacuum. 9.3 g of 2,2-dimethyl-4-butyltetrahydrothiopyran-4-ol (V) was synthesized as a colorless liquid:

B.p. 128° at 9 mm; n_D^{20} 1.4985; d_4^{20} 0.9880.
Found MR 59.99; calculated, 60.29.

6.300 mg substance: 7.119 mg $BaSO_4$.
3.200 mg substance: 3.622 mg $BaSO_4$.
Found %: S 15.68, 15.55.
$C_{11}H_{22}OS$. Calculated %: S 15.79.

Hydrogenation of 2,2-Dimethyl-4-vinylethynyltetrahydrothiopyran-4-ol.

10.6 g of the substance dissolved in 40 ml of alcohol was hydrogenated with hydrogen in the presence of 0.6 g of a palladium catalyst. 3.2 liters of hydrogen were absorbed as against the 3.9 liters required theoretically, after which the absorption of hydrogen was stopped. Then another 0.25 g of catalyst was added, and another 0.25 liter of hydrogen was absorbed during the next 12 hours. The usual treatment yielded 10 g of a substance with a b.p. of 142° at 15 mm; n_D^{20} 1.5092.

The synthesized product was dissolved in 40 ml of alcohol and rehydrogenated with hydrogen in the presence of 0.5 g of palladium catalyst. During 24 hours another 0.45 liter of hydrogen was absorbed. Distillation yielded 2.5 g of a substance with a b.p. of 119-126° at 4.5 mm; n_D^{24} 1.4982, and 7 g of a substance with a b.p. of 142° at 15 mm; n_D^{24} 1.5035.

Judging by the higher constants, the synthesized substance is not entirely pure thiopyranol (V), although it absorbed no more hydrogen when further hydrogenated with a Pd catalyst.

2,5-Dimethyl-4-vinylethynyltetrahydrothiopyran-4-ol.

5.8 g of 2,5-dimethyltetrahydrothiopyran-4-ol (VI) (m.p. 71°), dissolved in 30 ml of ether, was added to a solution of vinylacetylenemagnesium bromide, prepared from 2 g of magnesium, 8.5 g of ethyl bromide, 30 g of vinylacetylene, and 170 ml of ether. The reaction mass was boiled for 8 hours over a water bath, and the chilled solution was hydrolyzed with 17% hydrochloric acid. The usual treatment yielded 2,5-dimethyl-4-vinylethynyltetrahydrothiopyran-4-ol (VII), with a b.p. of 129° at 7 mm, which crystallized upon standing and fused at 32-37°. The synthesized

thiopyrenol (VII) is a mixture of two geometrical isomers. A product with a m.p. of 62.5-64° was isolated by repeated fractional crystallization from petroleum ether:

4.503 mg substance: 2.27 ml 0.02 N iodine solution.
3.267 mg substance: 1.64 ml 0.02 N iodine solution.
Found %: S 16.16, 16.09.
$C_{10}H_{18}OS$. Calculated %: S 16.32.

Dehydration of 2,5-dimethyl-4-vinylethynyltetrahydrothiopyran-4-ol.

15 g of the thiopyranol (VII) and 0.45 g of p-toluenesulfonic acid were heated in a 9-mm vacuum. Water began to be detached at 165-170°, and 5.3 g of a substance with a b.p. of 122-123° at 9 mm; n_D^{16} 1.5680, was driven off together with the water. The substance was extracted with ether and desiccated with sodium sulfate. Distillation yielded 2,5-dimethyl-4-vinylethynyltetrahydrothiopyran (VIII) or (IX), a yellow mobile liquid with an acrid odor, that breaks down upon standing.

B.p. 110-111° at 5.5 mm; n_D^{20} 1.5712; d_4^{20} 0.9995.
Found MR 58.53; calculated, 55.83.

4.830 mg substance: 13.008 mg CO_2; 3.355 mg H_2O.
5.435 mg substance: 14.597 mg CO_2; 3.820 mg H_2O.
Found %: C 73.49, 73.29; H 7.77, 7.86.
$C_{11}H_{14}S$. Calculated %: C 74.10; H 7.85.
3.838 mg substance: 1.980 ml 0.02 N iodine solution.
4.312 mg substance: 2.265 ml 0.02 N iodine solution.
Found %: S 16.54, 16.78.
$C_{11}H_{14}S$. Calculated %: S 17.97.

2,5-Dimethyl-4-butyltetrahydrothiopyran-4-ol.

14 g of 2,5-dimethyltetrahydrothiopyran-4-one, dissolved in 50 ml of ether, was gradually added to a solution of butylmagnesium chloride, prepared from 3 g of magnesium, 10 g of butyl chloride, and 50 ml of ether. The reaction mass was boiled for 23 hours. The solution, chilled with ice water, was hydrolyzed with 50 ml of 17% hydrochloric acid and extracted with ether. The ether solution was washed with soda, desiccated with magnesium sulfate, and distilled.

This yielded 6 g of 2,5-dimethyl-4-butyltetrahydrothiopyran-4-ol (X), a colorless, syrupy liquid:

B.p. 140° at 11 mm; n_D^{20} 1.5015; d_4^{20} 0.9902.
Found MR 60.14; calculated, 60.29.

3.614 mg substance: 1.760 ml 0.2 N iodine solution.
3.805 mg substance: 1.833 ml 0.2 N iodine solution.
Found %: S 15.62, 15.46.
$C_{11}H_{22}OS$. Calculated %: S 15.79.

2,3,6-Trimethyl-4-vinylethynyltetrahydrothiopyran-4-ol

33 g of 2,3,6-trimethyltetrahydrothiopyran-4-one (XI) was gradually added to a solution of vinylacetylenemagnesium bromide, prepared from 7 g of magnesium, 35 g of ethyl bromide, 20 g of vinylacetylene, and 170 ml of ether. The reaction mass was stirred for 4 hours while chilled with ice water, set aside to stand overnight, and again stirred for 1 hour the next day while the ether boiled energetically. While chilled with ice water, the product was hydrolyzed with 17% hydrochloric acid (200 ml). The usual treatment yielded 24 g of 2,3,6-trimethyl-4-vinylethynyltetrahydrothiopyran-4-ol (XII), a colorless, syrupy liquid:

B.p. 155-156° at 6 mm; n_D^{20} 1.5403; d_4^{20} 1.0345.
Found MR 63.71; calculated, 62.43.

5.239 mg substance: 5.719 mg $BaSO_4$.
4.042 mg substance: 4.450 mg $BaSO_4$.
Found %: S 14.99, 15.13.
$C_{12}H_{18}OS$. Calculated %: S 15.23.

Dehydration of 2,3,6-trimethyl-4-vinylethynyltetrahydrothiopyran-4-ol.

9.5 g of the thiopyranol (XII) was heated in the presence of pyrogallol with 3 g of finely ground potassium bisulfate in a 20-mm vacuum. Water began to split off at 200°, and 3.5 g of a substance with a b.p. of 158-162°, n_D^{18} 1.5572.

Desiccation and distillation yielded 2,3,6-trimethyl-4-vinylethynyldihydrothiopyran (XIII) or (XIV), a mobile yellow liquid with a disagreeable odor:

B.p. 146-147° at 7 mm; n_D^{20} 1.5600; d_4^{20} 0.9916.
MR found: 62.61; calculated, 60.44.

3.341 mg substance: 3.553 mg $BaSO_4$.
2.299 mg substance: 3.481 mg $BaSO_4$.
Found %: S 14.61, 14.49.
$C_{12}H_{18}S$. Calculated %: S 16.16.

2-Methyl-4-vinylethynylhexahydrothiochroman-4-ol.

22 g of 2-methylhexahydrothiochroman-4-one (XV) (m.p. 77-78°), dissolved in 50 ml of ether, was added gradually to a solution of vinylacetylenemagnesium bromide, prepared from 3.5 g of magnesium bromide, 15 g of ethyl bromide, 10 g of vinylacetylene, and 90 ml of ether. The reaction mass was boiled over a water bath for 6 hours with a reflux condenser left to stand overnight; the next day the product, chilled with ice water, was hydrolyzed with 17% hydrochloric acid (100 ml). The usual treatment yielded 4 g of the initial thiochromanone (XV), and 16.5 g of 2-methyl-4-vinylethynylhexahydrothiochroman-4-ol (XVI), a thick, colorless, glassy product, was synthesized:

B.p. 156° at 4 mm; n_D^{20} 1.5555; d_4^{20} 1.0866.
MR found 70.48; calculated 69.48.

7.040 mg substance: 18.325 mg CO_2; 5.305 mg H_2O.
8.780 mg substance: 22.835 mg CO_2; 6.745 mg H_2O.
Found %: C 71.04, 70.97; H 8.43, 8.59.
$C_{14}H_{20}OS$. Calculated %: C 71.19; H 8.47.

Dehydration of 2-methyl-4-vinylethynylhexahydrothiochroman-4-ol

3.5 g of the thiochromanol (XVI) and 0.1 g of p-toluenesulfonic acid were heated to 140° for 45 minutes in a 12-mm water-jet vacuum; the substance was then distilled in an oil-pump vacuum. This yielded 1.7 g of 2-methyl-4-vinylethynyltetrahydrothiochroman (XVIII) or (XIX), a mobile yellow liquid with an acrid odor:

B.p. 156° at 6 mm; n_D^{20} 1.5790; d_4^{20} 1.0330.
Found MR: 70.47; calculated 67.49.

7.080 mg substance: 19.771 mg CO_2; 5.257 mg H_2O.
Found %: C 76.21; H 8.31.
$C_{14}H_{18}S$. Calculated %: C 77.06; H 8.26.

The product darkened and grew thick when left to stand for two days in a test tube with a ground-glass stopper.

2-Methyl-4-butylhexahydrothiochroman-4-ol.

9 g of the thiochromanone (XV), dissolved in 30 ml of ether, was gradually added to a solution of butylmagnesium chloride, prepared with 1.5 g of magnesium, 5.5 g of butyl chloride, and 30 ml of ether. The reaction mass was boiled over a water bath for 9 hours and, while chilled, hydrolyzed with 17% hydrochloric acid (40 ml).

The usual treatment and vacuum distillation (4 mm) of the product yielded 1.9 g of the initial thiochromanone (XV) and 2.5 g of 2-methyl-4-butylhexahydrothiochroman-4-ol (XVII), consisting of colorless needles.

M.p. 79-80° and B.p. 153-156° at 4 mm.

3.408 mg substance: 2.[illegible] ml 0.01 N iodine solution.
3.423 mg substance: 2.[illegible] ml 0.01 N iodine solution.
Found %: S 12.64, 12.69.
$C_{14}H_{28}OS$. Calculated %: S 13.22.

In addition, 3 g of an intermediate fraction, consisting of a mixture of the initial thiochromanone (XV) and the thiochromanol (XVII), was recovered.

SUMMARY

When vinylacetylenemagnesium bromide is reacted with tetrahydro-γ-thiopyrones, we get a yield of some 80% of 4-vinylethynyltetrahydrothiopyran-4-ols. The latter are also synthesized by the condensation of tetrahydro-γ-thiopyrones with vinylacetylene in the presence of powdered potassium hydroxide, but the yield is lower (about 50%). Vacuum distillation of 4-vinylethynyltetrahydrothiopyran-4-ols with potassium bisulfate or p-toluenesulfonic acid yields about 60% of the corresponding dienynes (4-vinylethynyldihydrothiopyrans).

4-Butyltetrahydrothiopyran-4-ols are synthesized with high yields by the action of butylmagnesium chloride upon tetrahydro-γ-thiopyrones. The vinylacetylenic thiopyranols and thiopyrans can be hydrogenated in the presence of a Pd catalyst into the corresponding saturated compounds.

In contrast to the aliphatic and alicyclic dienynes, the dienynes of the thiopyran series cannot be hydrated and cyclized into the corresponding dienones and cyclopentenones.

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Received October 28, 1948.

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